THERMODYNAMICS OF ASSOCIATING SYSTEMS

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By

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ABSTRACT

The Peng-Robinson equation of state (PR EOS) is used with the infinite linear association model and the monomer-dimer association model as well as two different sets of mixing rules to result in four different forms of the equation of state. The reformulated Peng-Robinson equations of state have been used to calculate the vapor pressures and liquid densities of pure associating compounds such as alkanols, water, carboxylic acids etc. The vapor pressure and liquid density values calculated by means of the reformulated Peng-Robinson equations of state are in good agreement with the experimental data reported in the literature. Comparisons are also done with the Hong-Hu equation (Hong and Hu, 1989) and the Martin-Hou Association equation (AMH) (Nan *et al.*, 1997).

The application of the reformulated Peng-Robinson equations of state is extended to represent the vapor-liquid equilibria of associating systems. For a binary system in which only one component is an associating species, one binary interaction parameter is required to calculate the energy parameter of a mixture. For a binary system involving two associating species, an additional binary interaction parameter is used to adjust the association constant to give a good correlation of the experimental vapor-liquid equilibrium (VLE) values. The capabilities of different association-incorporated equations of state are compared with the Hong-Hu equation, the AMH equation and the Wilson equation. The results show that, in general, the reformulated Peng-Robinson equations of state are superior to the Wilson equation for all tested systems with the exception of alkanol+hydrocarbon systems and at least as good as the Hong-Hu equation and the AMH equation, although the number of tested systems from Hong and Hu (1989) and Nan *et al.* (2001a) are less than the one from the present work.

The excess molar enthalpies of the ethanol+*n*-hexane system at 298.15 K, 303.15 K and 313.15 K and the ethanol+cyclohexane system at 298.15 K are measured in an LKB 2107 microcalorimeter. Smooth representations of the results are described. The

comparisons of the experimental data measured at 298.15 K and 303.15 K for the ethanol+*n*-hexane system with those found in the literature are presented to test the reliability of the microcalorimeter. Additionally, new excess molar enthalpy data, measured at 298.15 K, have been reported for the ethanol+*n*-hexane+cyclohexane ternary system in the present work. Smooth representations of the results are described as well and used to construct contours of constant enthalpy on a Roozeboom diagram. Reasonable estimates of the excess molar enthalpies of the three constituent-binary mixtures can be obtained from both the Liebermann-Fried model and the Flory theory.

Finally, an attempt has been made to represent, simultaneously, both vapor-liquid equilibrium (VLE) and excess enthalpy behavior of the ethanol+*n*-hexane and ethanol+cyclohexane systems by using the Wilson equation and the reformulated Peng-Robinson equation of state on the basis of the infinite linear association model and the Heidemann-Prausnitz approach to defining mixture parameters. Both the reformulated Peng-Robinson equation of state and the Wilson equation are extended to predict the ethanol+*n*-hexane+cyclohexane ternary system at 298.15 K with the binary interaction parameters determined from the experimental vapor-liquid equilibrium (VLE) data of the three constituent-binary mixtures. The calculated results show that the reformulated Peng-Robinson equation of state is better than or as good as the Wilson equation in predicting the excess molar enthalpies of selected binary and ternary systems involving one associating species. However, quantitative discrepancies with the experimental data are observed.

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NOMENCLATURE

ENGLISH LETTERS

A	Helmholtz energy, $J \cdot mol^{-1}$
A	Component
A	Parameter of the Wilson equation, $cal \cdot mol^{-1}$
A	Coefficient in smoothing function of excess enthalpy
B	Component
$a, \hat{a}, \overline{a}, b, \hat{b}, \overline{b}$	Parameters of the equations of state
c	Binary parameter
C	Binomial coefficient in Equations (3.1.1.18 - 3.1.1.20)
E	Voltage reading, mV
E	Coefficients given by Equation (4.6), K
f	Fugacity, bar
f	Flow rate, $ml \cdot h^{-1}$
G	Gibbs free energy, $J \cdot mol^{-1}$
g	A quantity given by Equation (2.2.13)
H	Excess molar enthalpy, $J \cdot mol^{-1}$
K	Association constant
k	Binary interaction parameter
N	Number of experimental points
n	Number of moles, mol
OF	Objective function
P	Pressure, bar
Q	A quantity given by Equation (5.2.4)
Q	Interaction parameter
R	Universal gas constant, $l \cdot bar \cdot mol^{-1} \cdot K^{-1}$
R	A quantity given by Equations (3.1.1.27 - 3.1.1.29)
S	A quantity given by Equations (3.1.1.30 - 3.1.1.31)
s	Surface to volume ratio

s	Number of segments in a molecule in Equation (2.3.7)
s	Standard error
T	Absolute temperature, K
V	Total volume, cm^3
v	Apparent molar volume, $cm^3 \cdot mol^{-1}$
W	Heat effect
w	A quantity given by Equation (3.2.1)
x	Apparent mole fraction of component in liquid phase
Y	Attractive energy parameter in Equation (2.3.9)
y	Apparent mole fraction of component in vapor phase
Z	Compressibility factor
z	True mole fraction

GREEK LETTERS

α	Ratio of fugacity coefficient
α	Isobaric expansivity, $k \cdot K^{-1}$
β	A quantity given by Equation (3.2.6)
δ	Binary interaction parameter
ε	Calibration constant, $J \cdot s^{-1} \cdot V^{-1}$
ϕ	Hard core volume fraction
$\hat{\phi}$	Fugacity coefficient
φ	Volume fraction of monomer
γ	A quantity given by Equation (3.1.8)
γ	Activity coefficient
κ	Isothermal compressibility, $T \cdot Pa^{-1}$
λ	Energies of interaction between the molecules in the Wilson equation
π	A function of ξ in Equation (2.2.3)
θ	Site fraction
ϑ	Surface fraction

ρ	Density, $g \cdot cm^{-3}$
ω	Acentric factor
ξ	Reduced density
Λ	Adjustable parameter in the Wilson equation

SUPERSCRIPTS

0	Standard state
0	Baseline
assoc	Association term
ani	Anisotropic interaction term
att	Attraction term
ch	Chemical contribution
chain	Contribution from the formation of chains
E	Excess function
L	Liquid phase
LJ	Lennard-Jones interaction term
ph	Physical contribution
rep	Repulsion term
sat	Saturated
seg	Repulsion-dispersion contribution from monomeric segments
V	Vapor phase
*	Reduction parameter
^	Mixture property
-	Reduced quantity

SUBSCRIPTS

0	Quantity calculated ignoring association
1,2,…,j	Monomer, dimer,…, j-mer
A_1, B_1	Monomeric species

A, B, AB	Species
att	Attractive forces in Equation (2.2.1)
c	Chemical contribution
c	Critical property
cal.	Calculated values
exp.	Experimental data
hs	Hard sphere (repulsive forces) in Equation (2.2.1)
KW	KW model
M	Mixture
MD	Monomer-dimer model
MK	MK model
m	Mole property
p	Physical contribution
r	Reduced properties
T	True

ABBREVIATIONS

AAD	Average Absolute Deviation
ABPACT	Acid-Base version of the Perturbed-Anisotropic-Chain Theory
AEOS	Association Model + Equation of state
AMH	Martin-Hou Association
APACT	Associated-PACT
CPA	Cubic-Plus-Association
EOS	Equation of State
ERAS	Extended Real Associated Solution
HS-SAFT	Hard-Sphere-SAFT
LFAS	Lattice-Fluid Associated Solution
LLE	Liquid-Liquid Equilibrium
LJ-SAFT	Lennard-Jones-SAFT
PACT	Perturbed-Anisotropic-Chain Theory

PHCT	Perturbed Hard-Chain Theory
PPR	Reformulated Peng-Robinson
PR	Peng-Robinson
PVT	Pressure, Volume and Temperature
RK	Redlich-Kwong
RRMS	Relative Root Mean Square
SAFT	Statistical-Associating-Fluid-Theory
SLE	Solid-Liquid Equilibrium
SLP	Sanchez-Lacombe-Panayiotou
SPHCT	Simplified PHCT
SRK	Soave Redlich-Kwong
SSAFT	Simplified SAFT
SW-SAFT	Square-Well SAFT
VLE	Vapor-Liquid Equilibrium
VLLE	Vapor-Liquid-Liquid Equilibrium
TPT1	First order Thermodynamic Perturbation Theory

CHAPTER 1
INTRODUCTION

Many industrial systems contain molecules that interact with strong specific intermolecular forces such as hydrogen bonding. Hydrogen bonding results in highly polar covalent bonds when a molecule contains a hydrogen atom attached to either of the highly electronegative atoms O, N or F. Hydrogen-bonding interactions can occur between molecules of the same species or between molecules of different species. For the former hydrogen-bonding interaction, we define the behavior of same molecules to form polymers as association. One of the examples of compounds in which association occurs is ethanol, consisting of monomers, dimers, trimers etc., due to hydrogen-bonding interaction. Acetone is another good example in which association exists. Acetone molecules have both the London Force (between molecules of hydrogen and carbon dioxide for example) and the much stronger dipole-dipole force called a hydrogen bond. This explanation is supported by the fact that the molar enthalpy of vaporization of acetone is greater than that of butane (32.0 $kJ \cdot mol^{-1}$ vs. 24.3 $kJ \cdot mol^{-1}$). That is, more energy is required to vaporize one mole of acetone than one mole of butane. The Raman studies of Puranik (Pimentel and McClellan, 1960) shows the particular values for the effect of hydrogen bonding on the C—C (788 cm^{-1}) and C—H (2925 cm^{-1}) C==O (1723 cm^{-1}) stretching modes of acetone as well. In addition, chloroform, is an example in which hydrogen bonding effect exists. The infrared spectral studies (Pimentel and McClellan, 1960) provide a basis for concluding that hydrogen bonding occurs in chloroform. The fact that the characteristic increase in intensity of C—H stretch (ν_s) with hydrogen bond formation (i.e. chloroform is intensified several-fold) as compared to carbon tetrachloride, is more sensitive than frequency shift, indicates that an interaction specifically involves the hydrogen atom. Also the absorption coefficient measurements are consistent with the proposal that chloroform acts as a hydrogen bonding acid.

The behavior of molecules of different species to form complexes is defined as solvation. For instance, chloroform is solvated with acetone due to interaction between the hydrogen of the chloroform and the carbonyl oxygen of the acetone. Generally, we call systems in which association or solvation occurs associating systems.

The following example serves to explain how association effects lead to nonideal behavior by comparing the thermodynamic properties of two isomers such as ethanol and dimethyl ether. Both compounds have the same formula C_2H_6O. However, there is a strong association effects only in ethanol. Some properties of these two compounds are shown in Table 1.1 (Prausnitz, 1986).

As shown in Table 1.1, the boiling point, enthalpy of vaporization, and Trouton's constant of ethanol are larger than those of dimethyl ether. This is because of the additional cohesive forces in ethanol. As well, the solubility of ethanol in water is infinite whereas dimethyl ether is only partially soluble.

Evidence of the nonideal behavior resulting from solvation was illustrated by Campbell and Kartzmark (1960) by measuring and comparing the heats of mixing for acetone+chloroform and acetone+carbon tetrachloride mixtures. The authors found that the heats of mixing for the acetone+carbon tetrachloride mixture were positive, i.e., a small amount of heat resulting from the effect of physical intermolecular forces (dipole, induction, dispersion) was absorbed. On the other hand, the heats of mixing for the acetone+chloroform mixture were relatively large and negative. The results showed that although the effect of physical intermolecular forces caused some heat to be absorbed, the chemical heat effect was so big that it not only cancelled the physical contribution to the observed heats of mixing, but also caused heat to be released. This example provided strong evidence for hydrogen bonding between acetone and chloroform.

Table 1.1: Some Properties of the Isomers Ethanol and Dimethyl Ether

Properties	Ethanol	Dimethyl ether
Normal boiling point (°C)	78	-25
Enthalpy of vaporization at normal boiling point ($kJ \cdot mol^{-1}$)	42.6	18.6
Trouton's constant ($J \cdot mol^{-1} \cdot K^{-1}$)*	121	74.9
Solubility in water at 18°C and 1 bar (g/100g)	∞	7.12

*Trouton's constant is the entropy of vaporization at the normal boiling point.

As mentioned above, hydrogen-bonding systems exhibit deviation from ideal solution behavior. Studies of the thermodynamic properties of these systems are of importance in chemical industry applications. In the past several decades, many empirical and theoretical thermodynamic models have been proposed to represent the thermodynamic behavior of systems containing associating species. Among them, the equation of state (EOS) approach was chosen to represent the thermodynamic properties of pure associating compounds. The methods to treat the associating mixtures were based on both activity coefficient models and equations of state. The activity coefficient models have been used by researchers such as Nath and Bender (1983), Brandani and Evangelista (1984), Nagata (1985), Hofman and Nagata (1987). They developed the associated solution theories by combining the chemical theory with activity coefficient methods to correlate phase equilibria and excess properties of binary and ternary systems containing associating components.

More effort has been made to extend the applicability of EOS to obtain accurate representations of thermodynamic properties for associating mixtures. Heidemann and Prausnitz (1976) were the first authors to incorporate the infinite linear association model with a pressure-volume-temperature-composition physical property relationship to develop a closed-form EOS for associating species. The resulting equation was capable of representing the critical isotherms of argon, water, and acetonitrile with all relevant parameters determined from the critical properties of the species.

The work of Heidemann and Prausnitz (1976) led to the development of several new EOS. The success obtained by Hu *et al.* (1984) in the development of a closed-form EOS is remarkable. In their work, a systematic derivation was presented for the Helmholtz free energy function of the associating systems. Some simplifying assumptions such as infinite linear association and uniform chemical equilibrium constants for the chemical reaction equilibria were used to develop an EOS. The EOS was used to correlate Henry's constant for nonpolar solutes in water. The correlation was only partly successful for mixtures containing molecules that were close in size. The approach by Hu *et al.* (1984) was subsequently used in the work of Hong and Hu (1989), who incorporated the monomer-dimer model with the Redlich-Kwong (Redlich and Kwong, 1949) EOS to develop a closed-form EOS. The Hong-Hu EOS was superior in

most cases to other more complicated association models and the usual activity coefficient methods in representing the vapor-liquid equilibria for non-aqueous mixtures involving associating and non-associating molecules. Zhao and Hu (1990) developed a similar equation and applied it to the correlations of excess properties of associating mixtures.

In this work, we have applied the approach proposed by Hu *et al.* (1984) to the PR EOS by incorporating it with either an infinite linear or a monomer-dimer association model to develop the reformulated equations of state. Serving as an account of the work carried out in this study, this thesis is divided into eight Chapters:

Chapter 1 is an introduction to this thesis, including background material. The objective of this research will be focus on extending the applicability of the PR EOS to the pure associating substances and the associating mixtures involving alkanols, water, carboxylic acids and etc.

Chapter 2 provides a thorough literature review to give the reader knowledge necessary to understand different models developed for associating systems.

Chapter 3 describes the development of models. Emphasis is placed on the development of reformulated equations of state that incorporate either an infinite linear or a monomer-dimer association model and two different sets of mixing rules into the original PR EOS.

In Chapter 4, the applicability of the reformulated equations of state has been assessed by correlating the vapor pressures and liquid densities of pure associating compounds and comparing with the experimental data from the literature.

Chapter 5 is devoted to extending the reformulated equations of state to the representation of the vapor-liquid equilibria of associating mixtures. The calculated results are compared with the results obtained from the existing models.

Chapter 6 describes the measurement of new excess molar enthalpies of associating mixtures involving ethanol, *n*-hexane and cyclohexane at 298.15 K. A comparison of the experimental data with the estimated excess molar enthalpies of its constituent-binary mixtures obtained from both the Liebermann-Fried model and the Flory theory is presented in this Chapter. The predictive capability of the reformulated equation developed from this work will be verified by comparing the new excess molar

enthalpy data of ethanol+*n*-hexane+cyclohexane at 298.15 K measured from this work with the predicted results from the reformulated equation in next Chapter.

Chapter 7 describes representations of both VLE and excess enthalpy behavior of selected binary systems by using the Wilson equation and the selected reformulated EOS. A comparison of the experimental data with calculated results obtained from both the Wilson equation and the reformulated EOS is presented. The applicability of the selected reformulated EOS is further extended to prediction of the excess molar enthalpies of the ternary mixture that have been measured in this work.

Chapter 8 summarizes the research performed and the results. Some recommendations that can be done to improve on aspects of this study are also presented.

CHAPTER 2
LITERATURE REVIEW

The accurate description of the thermodynamic properties of associating systems is of importance to the chemical industry. During the past several decades, a number of extensive and thorough studies have been carried out by different researchers with the aim of developing models to represent the thermodynamic properties of associating systems. A variety of models based on chemical theory, perturbation theory, or lattice/quasi-chemical theory can be found in the literature. In this Chapter, some selected models are divided into the above groups and briefly discussed.

2.1 Extended Real Associated Solution Model (ERAS)

Dolezalek (1908) was among the first to propose that any deviation from ideal behavior could be related to the formation of new species. The modern use of chemical theory began with Kretschmer and Wiebe (1954), who used the Flory-Huggins equation (Flory, 1942) as a basis and a continued association model for polymerization reaction to derive the expressions for Helmholtz free energy, energy of mixing and excess entropy of solutions of alkanols in non-associating solvents. The derived equations were capable of successfully representing the energy of mixing and excess entropy of the ethanol+methylcyclohexane system. This work was later supplemented and put in a more complete form by Renon and Prausnitz (1967), who developed the real associated solution model on the basis of Flory's lattice model (Flory *et al.*, 1964). The model was used to represent the excess Gibbs energy and excess enthalpy of an alcohol+hydrocarbon system with good accuracy, especially at high alcohol concentrations. Although the real associated solution model was capable of describing the excess Gibbs energy and excess enthalpy, it could not be used to predict the excess volume and other related properties because of the restrictions imposed by the rigid lattice approach.

Heintz (1985) developed the so-called Extended Real Associated Solution Model (ERAS) by combining the extended version of the Kretschmer-Wiebe associated solution model (Kretschmer and Wiebe, 1954) with Flory's theory (Flory *et al.*, 1964). The derivation of the ERAS model starts with the partition function of a mixture of a self-associating (A) molecule (say, alkanol) and an inert molecule (B). The excess functions G^E, H^E and V^E can be split into a chemical and a physical contribution term. The excess enthalpy is

$$H^E = H_c^E + H_p^E \tag{2.1.1}$$

where the terms, H_c^E and H_p^E account for the chemical and physical contributions, respectively, and are defined by the following equations:

$$H_c^E = K_A \Delta h_A^* x_A \left(\varphi_{A1} - \varphi_{A1}^0\right) - x_A \frac{p_M^*}{\overline{V}_M} K_A \Delta v_A^* \left(\varphi_{A1} - \varphi_{A1}^0\right) \tag{2.1.2}$$

$$H_p^E = \left(V_A^* x_A + V_B^* x_B\right)\left(\phi_A \frac{p_A^*}{\overline{V}_A} + \phi_B \frac{p_B^*}{\overline{V}_B} - \frac{p_M^*}{\overline{V}_M}\right) \tag{2.1.3}$$

The excess Gibbs energy G^E and excess volume V^E are expressed in forms similar to that for H^E:

$$G^E = G_c^E + G_p^E \tag{2.1.4}$$

where

$$G_c^E = RT\left[x_A \ln \frac{\varphi_{A1}}{\varphi_{A1}^o . x_A} + x_B \ln \frac{\phi_B}{x_B} + K_A x_A \left(\varphi_{A1} - \varphi_{A1}^o\right)\right] \tag{2.1.5}$$

$$G_p^E = H_p^E - T\left(V_A^* x_A + V_B^* x_B\right)\left\{\vartheta_B \phi_A Q_{AB} - 3\phi_B \frac{p_B^*}{T_B^*} \ln\left(\frac{\overline{V}_B^{1/3} - 1}{\overline{V}_M^{1/3} - 1}\right) - 3\phi_A \frac{p_A^*}{T_A^*} \ln\left(\frac{\overline{V}_A^{1/3} - 1}{\overline{V}_M^{1/3} - 1}\right)\right\} \tag{2.1.6}$$

and

$$V^E = V_c^E + V_p^E \tag{2.1.7}$$

where

$$V_c^E = \overline{V}_M x_A K_A \Delta v_A^* \left(\varphi_{A1} - \varphi_{A1}^0\right) \tag{2.1.8}$$

$$V_p^E = \left(V_A^* x_A + V_B^* x_B\right)\left(\overline{V}_M - \phi_A \overline{V}_A - \phi_B \overline{V}_B\right) \tag{2.1.9}$$

K_A is the association constant of the associating molecule A, which is obtained by adjusting the ERAS model to best match the experimental excess properties and the enthalpy of vaporization of pure associating compounds. Δh_A^* is the hydrogen bonding energy of the associating molecule A, the value of which is taken as –25 kJ·mol^{-1} for all alkanols (Renon and Prausnitz, 1967). φ_{A1} and φ_{A1}^0 are the volume fractions of the monomeric alkanol species in the solution and in the pure alkanol, respectively, and are related to the association constant K_A, as follows:

$$\varphi_{A1} = \frac{2K_A\phi_A + 1 - \sqrt{4K_A\phi_A + 1}}{2K_A^2\phi_A} \tag{2.1.10}$$

$$\varphi_{A1}^0 = \frac{2K_A + 1 - \sqrt{4K_A + 1}}{2K_A^2} \tag{2.1.11}$$

with

$$\phi_A = \frac{x_A V_A^*}{x_A V_A^* + x_B V_B^*} = 1 - \phi_B \tag{2.1.12}$$

ϕ_A and ϕ_B are the hard core volume fractions of the species A and B. V_A^* and V_B^* are the hard core volumes of species A and B, respectively, which can be calculated from the thermal expansion coefficients of the pure substances. T_A^* and T_B^* can be calculated from the reduced temperatures of species A and B, respectively. p_A^* and p_B^* are related to the isothermal compressibility, and p_M^* can be obtained by using the mixing rules given by the following equation:

$$p_M^* = p_A^*\phi_A + p_B^*\phi_B - \phi_A\vartheta_B X_{AB} \tag{2.1.13}$$

The reduced parameters of the pure substances have the following definitions:

$$\overline{V}_i = V_i^{mol} / V_i^* \tag{2.1.14}$$

$$\overline{T}_i = T_i / T_i^* \tag{2.1.15}$$

$$\overline{p}_i = p_i / p_i^* \tag{2.1.16}$$

The surface fraction ϑ_B, of species B in the mixture is defined as

$$\vartheta_B = \frac{s_B / s_A \phi_B}{\phi_A + s_B / s_A \phi_B} \tag{2.1.17}$$

where s_A and s_B are the surface to volume ratios of species A and B, respectively. One of the adjustable parameters, Δv_A^*, in Equation (2.1.2) is the association volume, which is adjusted to the experimental excess volume data of each system. The two remaining adjustable parameters X_{AB} in Equation (2.1.13) and Q_{AB} in Equation (2.1.6), can be evaluated by adjusting them to match the experimental excess enthalpy values and VLE or LLE data of the mixtures.

The ERAS model has been successfully applied to the simultaneous descriptions of the excess Gibbs energy, excess enthalpy and excess volume of alcohol+alkane systems. Funke *et al.* (1989) applied the ERAS model to the excess function predictions of amine+hydrocarbon mixtures. Kaur *et al.* (1989) first used the ERAS model to calculate the excess functions of the cycloalkanol+*n*-alkane mixtures and later on, to calculate the excess volume of alkanol+*n*-alkane mixtures (Kaur *et al.*, 1991). Additionally, the ERAS model has been used to describe the excess properties of the amine+alkane mixtures by Reimann and Heintz (1991), 1-alkanol+1-alkane mixtures by Bender and Heintz (1993), 1-alkanol+1-alkene and 1-alkanol+1-alkyne mixtures by Letcher *et al.* (1995). More recently, Pina and Francesconi (1998) used the ERAS model to calculate the excess properties of the 1-alkanol+acetonitrile mixtures. Furthermore, Bender *et al.* (1991) extended the application of the ERAS model to ternary mixtures involving two associating components (alkanol, amine) and one inert component (alkane).

In this work, the applicability of the ERAS model has been verified by using it to represent the excess properties of selected alkanol+alkane systems. The comparisons of the calculated results with the experimental data for selected systems at the temperatures indicated are presented in Appendix C for reference.

2.2 Association-incorporated van der Waals-type Equations

Heidemann and Prausnitz (1976) developed a van der Waals-type equation of state that incorporates an association model. The basic concept of the van der Waals equation (van der Waals, 1890) is that the pressure is a sum of two terms:

$$P = P_{hs} + P_{att} \qquad (2.2.1)$$

where subscripts *hs* and *att* stand for hard sphere (repulsive forces) and attractive forces, respectively. The first contribution in Equation (2.2.1) can be rewritten in terms of compressibility:

$$P_{hs} = n_T RTz_{hs} / V \tag{2.2.2}$$

and the attractive-force contribution to the pressure is rewritten in the following form:

$$P_{att} = -\left(\hat{a} / \hat{b}^2\right)\pi_{att}(\xi) \tag{2.2.3}$$

where the reduced density ξ is defined as

$$\xi = n_T \hat{b} / V \tag{2.2.4}$$

The volume V is expressed as

$$V = vn_0 \tag{2.2.5}$$

π_{att} is a function of ξ; the terms n_T and n_0 are the true mole number and the apparent mole number which is the total number of moles that would exist if there were no association, respectively. Let's take one example as an explanation of the term n_T and n_0. A mixture consisting of four moles of species A and six moles of species B is "prepared" gravimetrically. So the "apparent" total mole number, n_0 is ten moles. If A is non-associating and B undergoes monomer-dimer equilibrium, then the "true" total mole number, n_T is smaller than ten. In particular, if two moles of the B dimerize to form one mole of B_2, then the true total mole number n_T, is 4+4+1=9. We can never prepare a mixture with specified "true" total mole number, but we can always prepare mixtures with specified "apparent" total mole number.

The constant $\hat{a}$, which essentially is that of the original van der Waals equation, depends on the true composition, *z*, of the mixture (here, a pure fluid is considered to be a mixture of monomers, dimers, trimers, etc.). Another parameter $\hat{b}$, which is proportional to the volume of the hard-sphere molecules, depends on the true composition of the mixture as well. The value of $\hat{b}$ would be expressed as $\pi N_{AV}\sigma^3/6$ if all molecules were monomers where N_{AV} is the Avogadro number and σ is the collision diameter. Heidemann and Prausnitz (1976) introduced the simplifying

assumptions that the molecular parameters of the associated species j, which is formed of j monomers, are related to those of the monomer by the following equations:

$$a_j = j^2 a \tag{2.2.6}$$

$$b_j = jb \tag{2.2.7}$$

Upon substituting the above relations for the associating species into the conventional van der Waals-type mixing rules given by

$$\hat{a} = \sum_i \sum_j z_i z_j (a_i a_j)^{0.5} \tag{2.2.8}$$

$$\hat{b} = \sum_k z_k b_k \tag{2.2.9}$$

one obtains the following equations, which serve to represent the relationships between the overall parameters of the associated species, $\hat{a}$, $\hat{b}$, and the monomer parameters a and b

$$\hat{a} = (n_0 / n_T)^2 a \tag{2.2.10}$$

$$\hat{b} = (n_0 / n_T) b \tag{2.2.11}$$

The resulting equation is expressed in the following form:

$$P = (n_T / n_0)(RT / b)\xi z_{hs} - (a / b^2)\pi_{att} \tag{2.2.12}$$

where $\xi = b / v$

The general form of the ratio n_T / n_0 is obtained by solving both chemical equilibrium and material balances:

$$n_T / n_0 = \frac{2}{1 + \sqrt{1 + (4KRT / b)\xi \exp(g)}} \tag{2.2.13}$$

where z_{hs}, π_{att} and g in Equations (2.2.12) and (2.2.13) are the functions of reduced density, ξ, and K is the chemical equilibrium constant. Heidemann and Prausnitz (1976) applied different forms of equations for z_{hs}, π_{att} and g to decide the best functionality to use. For example, if the Carnahan-Starling (1969) equation is used to express z_{hs} and g and the van der Waals form is adopted to express π_{att}, then

$$z_{hs} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \tag{2.2.14}$$

$$g = \frac{4\xi - 3\xi^2}{(1-\xi)^2} \tag{2.2.15}$$

$$\pi_{att} = \xi^2 \tag{2.2.16}$$

and if the RK EOS is used to express π_{att}, then

$$\pi_{att} = \frac{\xi^2}{1+4\xi} \tag{2.2.17}$$

They also stated that a possible useful form for π_{att} in their preliminary data-reduction work was

$$\pi_{att} = \xi^2(1-4\xi) \tag{2.2.18}$$

Heidemann and Prausnitz (1976) substituted Equations (2.2.13), (2.2.14) and (2.2.18) into Equation (2.2.12) to obtain a closed-form equation of state that was shown to be capable of representing the critical isotherms of argon, water, and acetonitrile well with all relevant parameters determined from only the critical properties of the species.

The hypotheses of Heidemann and Prausnitz (1976) were later used by other researchers. Hu *et al.* (1984) proposed a different formula for estimating the energy parameters for the associated species and applied the equation of state method to represent the phase behavior of associating mixtures. The mixing rules they presented are shown below:

$$\hat{a} = (n_0 / n_T)\sum_k \sum_l x_k x_l (a_k a_l)^{0.5}(1-k_{kl}) = (n_0 / n_T)\bar{a} \tag{2.2.19}$$

$$\hat{b} = (n_0 / n_T)\sum_k x_k b_k = (n_0 / n_T)\bar{b} \tag{2.2.20}$$

The indices k and l refer to all the species in the mixture as if there were no association. $\bar{a}$ and $\bar{b}$ serve to represent the relationships between the overall parameters of mixtures and those of the pure species as if there were no association.

Hu *et al.* (1984) chose the Carnahan-Starling equation to represent the hard-sphere contribution and the RK equation for the attractive-potential contribution to develop the expression for the Helmholtz free energy. The Carnahan-Starling/Redlich-Kwong closed-form equation could be readily obtained in terms of the thermodynamic relation. It was successfully used to correlate Henry's constants of gases in water over a wide temperature range. However, they also concluded that the equation used in their

calculations did not give satisfactory results for binary mixtures such as water+benzene in which components differ markedly in size. Subsequently, Hong and Hu (1989) applied the approach developed by Hu *et al.* (1984) and incorporated the monomer-dimer model with the RK equation of state. The final closed-form equation of state with chemical association built-in was expressed as

$$P = \frac{n_T}{n_0}\left[\frac{RT}{v-\bar{b}} - \frac{\bar{a}}{v(v+\bar{b})}\right] \tag{2.2.21}$$

where the ratio n_T / n_0 could be calculated by solving the chemical equilibria and material balances simultaneously. The Hong-Hu equation (Hong and Hu, 1989) was shown, in most cases, to be superior to other more complicated association models and conventional activity coefficient methods in representing the vapor-liquid equilibria of non-aqueous mixtures involving associating and non-associating molecules.

Twu *et al.* (1993a) first incorporated the monomer-dimer chemical equilibrium model into cubic equations of state to model systems containing carboxylic acids. Later, using the same approach as the one proposed by Twu *et al.* (1993a), a monomer-hexamer chemical equilibrium model because the vapor of hydrogen fluoride exists primarily as monomer and hexamer, was built into a cubic equation of state to result in a closed-form equation of state (Twu *et al.*, 1993b). The developed model has been used to calculate the fugacity coefficient, vapor compressibility factor, heat of vaporization and excess enthalpy of hydrogen fluoride with good accuracy.

Nan *et al.* (1997) developed the Martin-Hou Association (AMH) equation of state by incorporating the infinite linear association model and monomer-dimer association model into the Martin-Hou equation of state (Martin and Hou, 1955). These authors used the AMH equation of state with a set of parameter scaling rules similar to those given by Equations (2.2.6) and (2.2.7) to correlate the thermodynamic properties of associating systems. The AMH equation of state is relatively complex in comparison to the simple equation of state as it involves nine parameters. Although the AMH equation of state (Nan *et al.*, 2001a) can be applied to the thermodynamic calculations of pure associating compounds and has been extended to the calculations of vapor-liquid equilibria of mixtures involving associating molecules, Nan *et al.* (2001a) indicated that the calculated results obtained from the AMH equation of state were not satisfactory for

aqueous systems because of unsuitable mixing rules or association models in the development of the model for water.

Although many authors have made significant improvement to the volumetric property and phase behavior calculation of associating systems by using the equation of state approach, no attempt had been made to correlate the excess properties until 1990.

Zhao and Hu (1990) applied the approach proposed by Hu *et al.* (1984) to correlate the excess properties of alcohol+alkane and alcohol+carboxylic acid mixtures with good accuracy. Nan *et al.* (2001b) used the AMH equation of state to calculate the excess enthalpies of alcohol+hydrocarbon and alcohol+alcohol mixtures. The results obtained served to indicate that the AMH equation of state was reliable.

2.3 Associated Perturbed Anisotropic Chain Theory (APACT)

Equations (2.2.12) and (2.2.21) represent two distinct forms of an equation of state for associating mixtures. Hu *et al.* (1984) modified the original van der Waals equation and Carnahan-Starling equation by means of correcting for both the repulsive pressure term and the attractive pressure term whereas Heidemann and Prausnitz (1976) proposed an approach to modify only the repulsive pressure term in a van der Waals-type equation. In both approaches, the correction factor is the ratio of the true number of moles n_T to the apparent number of moles n_0. In addition, other researchers such as Ikonomou and Donohue (1986, 1987, 1988), Economou *et al.* (1990), Economou and Donohue (1991, 1992), Economou and Peters (1995), Economou *et al.* (1995), Economou and Donohue (1996) and Campbell *et al.* (1992) proposed closed-form equations for associating systems that involve this correction factor. The explicit expression for the ratio n_T / n_0 in terms of molar volume, temperature, etc. depends on the form of the original equation of state for non-associating systems and how the parameters are calculated for the associating species.

Ikonomou and Donohue (1986) incorporated the infinite linear and monomer-dimer association models into the PACT (Vimalchand and Donohue, 1985) equation to derive the Associated Perturbed Anisotropic Chain Theory (APACT) equation. The APACT equation is written in terms of the compressibility factor as a sum of the contributions from the repulsive, attractive and associative interactions:

$$Z = 1 + Z^{rep} + Z^{att} + Z^{assoc} \tag{2.3.1}$$

where the repulsive term, Z^{rep}, and the attractive term, Z^{attr}, are given by Vimalchand and Donohue (1985), Vimalchand *et al.* (1986) and Economou *et al.* (1995) as

$$Z^{rep} = \langle c \rangle \frac{\xi(4-2\xi)}{(1-\xi)^2} \tag{2.3.2}$$

$$Z^{att} = Z_1^{LJ} + Z_2^{LJ} + \ldots + Z_2^{ani} + Z_3^{ani} + \ldots \tag{2.3.3}$$

where $\langle c \rangle$ is the number of external degrees of freedom and the reduced density, ξ, is defined as

$$\xi = \frac{\tau}{\langle \tilde{v} \rangle} = \frac{\tau}{V / n_T} \tag{2.3.4}$$

The term τ takes the value of $\pi\sqrt{2}/6$. All quantities in angular brackets represent mixture properties. As shown in Equation (2.3.3), the attractive term can be expressed as a sum of Lennard-Jones interaction terms, Z^{LJ}, and anisotropic interaction terms, Z^{ani}. The association term, Z^{assoc}, in Equation (2.3.1) is represented by (Ikonomou and Donohue, 1986; Economou and Donohue, 1991, 1992)

$$Z^{assoc} = \frac{n_T}{n_0} - 1 \tag{2.3.5}$$

The APACT equation has been applied to correlate the thermodynamic properties of pure associating compounds (Ikonomou and Donohue, 1986; Vimalchand *et al.*, 1988) and yielded considerable improvement on the phase equilibrium prediction when compared with the PACT (Vimalchand and Donohue, 1985) equation for associating systems involving one associating species (Ikonomou and Donohue, 1986, 1988). Moreover, Economou *et al.* (1990) extended the APACT equation to treat multicomponent mixtures where Lewis acid-base interactions occur and developed the Acid-Base version of the Perturbed-Anisotropic-Chain Theory (ABPACT). They have found that the binary VLE results obtained from the ABPACT equation were better than those calculated on the basis of the PR EOS, UNIFAC and the original APACT. Inspired by the work of Ikonomou and Donohue (1986), Campbell *et al.* (1992) derived the expression for the correction factor using an approach introduced by Nagata and Ohtsubo (1986) and presented a general closed-form equation of state for binary

associating mixtures. The general expression can be reduced to the analytic equations for special cases whereas no general analytic solution to the resulting equation was found. Meanwhile, Economou and Donohue (1992) extended the APACT equation to compounds with three associating sites per molecule. The accuracy of the three-site APACT equation has been tested for aqueous mixtures with polar and non-polar molecules over a large range of temperatures and pressures. In particular, the three-site APACT equation provided good liquid-liquid equilibrium (LLE) estimates of water+hydrocarbon systems. In addition, Smits *et al.* (1994) applied the APACT equation to the PVT behavior of pure water for pressures up to 50000 bar, including the near-critical region with good agreement between the experimental data and the calculated results with APACT. They concluded that the three-site was better than the two-site APACT equation in the calculation of volumetric properties, although the difference between these two equations was small. Economou and Peters (1995) also applied the APACT equation to the correlations of the vapor pressures and the saturated vapor and liquid densities of pure hydrogen fluoride from the triple point to the critical point. They have also used the APACT equation to predict the phase equilibria of hydrogen fluoride+chlorofluorocarbons (CFCs) and hydrogen fluoride+HCl mixtures. Meanwhile, Economou *et al.* (1995) further used the APACT equation to account for the strong dipole-dipole interactions between water and salt molecules and applied it to the phase equilibrium calculations of water+salt systems.

Although the APACT equation is powerful in representing the properties of associating systems, the APACT equation is mathematically complex. A much simpler so-called COMPACT equation (Ikonomou and Donohue, 1987) has been developed using local composition model (Lee *et al.*, 1985), which was later extended to model non-spherical molecules. The extended local composition model (LLS equation) is referred to as the Simplified PHCT (SPHCT). The COMPACT equation is derived on the basis of the Simplified PHCT (SPHCT). The SPHCT is used as a starting point to derive the COMPACT equation as follows:

$$\frac{PV}{n_T RT} = 1 + \langle c \rangle \frac{\xi(4-2\xi)}{(1-\xi)^3} + \frac{Z_M \langle cv^* Y \rangle}{v + \langle v^* Y \rangle} \qquad (2.3.6)$$

where

$$\langle v^* \rangle = \sum_{j=1}^{\infty} z_j s_j \sigma_{jj}^3 / \sqrt{2} \tag{2.3.7}$$

$$\langle c \rangle = \sum_{j=1}^{\infty} z_j c_j \tag{2.3.8}$$

$$\langle cv^* Y \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} z_i z_j c_i v_j^* \left[\exp\left(\varepsilon_{ij} q_i / 2 c_i kT\right) - 1 \right] \tag{2.3.9}$$

There are five molecular parameters in Equations (2.3.7 - 2.3.9), the inter-segment potential energy well depth, ε; the segmental radius, σ; the external degrees of freedom per molecule, c; the number of segments in a molecule, s and the surface area of a molecule relative to a spherical segment, q. A set of simple expressions similar to those proposed by Heidemann and Prausnitz (1976) are used to describe the relationships between the molecular parameters for each j-mer (subscript j) and those of the monomer (subscript 1) for associating species:

$$c_j = jc_1 \tag{2.3.10}$$

$$s_j = js_1 \tag{2.3.11}$$

$$q_j = jq_1 \tag{2.3.12}$$

$$\varepsilon_{ij} = \varepsilon_{11} \tag{2.3.13}$$

$$\sigma_{jj}^3 = \sigma_{11}^3 \tag{2.3.14}$$

Substitution of Equations (2.3.10 - 2.3.14) into Equation (2.3.6) leads to the closed-form equation of state given by

$$\frac{PV}{n_0 RT} = \frac{n_T}{n_0} + c_1 \frac{\xi(4-2\xi)}{(1-\xi)^2} + \frac{Z_M \langle c_1 v_1^* Y_1 \rangle}{v/n_0 + \langle v_1^* Y_1 \rangle} \tag{2.3.15}$$

Preliminary results from the COMPACT equation showed that it presented a significant improvement over the SPHCT equation in the prediction of phase equilibria for many hydrogen-bonding mixtures whereas the APACT equation worked better than the COMPACT equation in the prediction of phase equilibria of highly complex systems such as water+butane at high pressures.

2.4 Association-incorporated Equations of State (AEOS)

Encouraged by the work of Ikonomou and Donohue (1986), Anderko (1989a) used a similar approach to propose new equations (AEOS = Association Model + Equation of State). The basic idea to develop the new equations is that the compressibility factor of an associating fluid could be written as the sum of physical and chemical contributions. The physical contribution is represented by the original equation of state for non-associating molecules while the chemical contribution is represented by the difference between the ratio n_T / n_0 and unity. The compressibility factor can be expressed in the following form:

$$Z = Z^{ph} + Z^{ch} - 1 \tag{2.4.1}$$

where the equation of state developed by Yu *et al.* (1987) is chosen to serve for the physical contribution term, Z^{ph}:

$$Z^{ph} = \frac{V}{V-b} - \frac{a(T)V}{RT\left[V(V+c)+b(3V+c)\right]} \tag{2.4.2}$$

The parameters $a(T)$, b and c in Equation (2.4.2) are computed from the critical properties and acentric factor of pure components. The chemical contribution to the compressibility factor is expressed in three forms on the basis of the MK, KW (Kehiaian and Treszczanowicz, 1970), and monomer-dimer models, respectively:

$$Z^{ch}_{MK} = \frac{2}{1+\sqrt{1+4KRT/V}} \tag{2.4.3}$$

$$Z^{ch}_{KW} = \frac{1-KP_{A1}}{1+KP_{A1}} \tag{2.4.4}$$

$$Z^{ch}_{MD} = \frac{2-2RTK/V}{1-4RTK/V+\sqrt{1+8RTK/V}} \tag{2.4.5}$$

where P_{A1} is the partial pressure of monomer of associating species A.

The AEOS is applicable to the phase equilibrium (VLE, SLE, LLE) calculations in various types of mixtures containing water/alcohols and hydrocarbons (Anderko, 1989a, 1989b, 1989c, 1989d, 1990a, 1990b, 1991, 1992; Wiśniewska and Malanowski, 1990).

Lencka and Anderko (1993) were the first authors to use the PR EOS coupled with the method proposed by Anderko (1989a) to develop a new equation. The

developed equation is written as a sum of the physical and chemical contributions based on the original PR EOS and the distribution function, respectively:

$$Z = Z^{ph} + Z^{ch} - 1 \tag{2.4.6}$$

where the term for the physical contribution is given by

$$Z^{ph} = \frac{v}{v-b} - \frac{a(T)v}{RT\left[v(v+b)+b(v-b)\right]} \tag{2.4.7}$$

and the term for the chemical contribution is

$$Z^{ch} = F\left(\frac{RTK}{v}\right) \tag{2.4.8}$$

F is an algebraic function which depends on the distribution function $f(j)$.

The developed equation in the form of Equation (2.4.6) has been successfully used to represent the pure component data of hydrogen fluoride and predict phase equilibria of hydrogen fluoride+halocarbon systems. Other researchers who have used this approach to extend the application of the PR EOS include Kang (1999), and Lee and Kim (2001).

Kang (1999) applied the model presented by Lencka and Anderko (1993) to the VLE correlations of the propane+hydrogen fluoride mixture. The correlation was found to be in good agreement with the experimental data whereas the calculated equilibrium pressures at much diluted compositions of hydrogen fluoride, below about 0.01 mole fraction, were shown to be rather higher than the experimental values.

Lee and Kim (2001) used the same approach as the one proposed by Lencka and Anderko (1993) to develop an equation of state for hydrogen fluoride. The physical contribution in Equation (2.4.6) could be expressed by the PR EOS whereas the chemical contribution in Equation (2.4.6) was calculated from material balance instead of Equation (2.4.8). The resulting equation was capable of correlating the vapor pressures, the saturated liquid and vapor densities of hydrogen fluoride from the triple point to critical point with good accuracy. The developed equation together with the Wong–Sandler mixing rule as well as the van der Waals one-fluid mixing rule has been applied to the phase equilibrium correlations of binary mixtures involving hydrogen fluoride+HCl, hydrogen fluoride+HCFC-124, hydrogen fluoride+HFC-134a, hydrogen fluoride+HFC-152a, hydrogen fluoride+HCFC-22, and hydrogen fluoride+HFC-32.

Comparing the new equation of state with the van der Waals one-fluid mixing rule, the new one incorporating the Wong–Sandler mixing rule gave better results.

Karan *et al.* (1998) used the PR EOS to describe the phase behavior of elemental sulfur and the solubility of sulfur in natural gas mixtures. The sulfur was treated as if it were the single molecule S_8 under all conditions. The model developed for sulfur was successfully used to obtain excellent liquid volumes and vapor pressures of sulfur. However, the model failed to predict the vapor density and the heat of vaporization of sulfur at higher temperatures. Later on, Heidemann *et al.* (2001) applied a chemical equilibrium model and the PR EOS to model the phase behavior of natural gases containing elemental sulfur. The sulfur was treated as a mixture of eight species, S_1 through S_8 instead of only single species S_8 in earlier work (Karan *et al.*, 1998). They regarded all of the other species as being formed from the S_8 molecule via the chemical equilibrium reactions. Therefore, only the S_8 parameters have to be fitted to pure sulfur vapor pressure and liquid density data. The developed model showed the correct qualitative behavior of the heat of vaporization of liquid sulfur and considerable improvement on vapor density of sulfur over the earlier model (Karan *et al.*, 1998). The model represented a good correction of binary data for sulfur and natural gas components containing hydrogen sulfide which was a mixture component including the equilibrium formation of the sulfanes from H_2S_2 to H_2S_9, carbon dioxide, methane, and nitrogen.

2.5 Statistical Associating Fluid Theory (SAFT)

While much progress has been made in the development of the equations of state derived from chemical theory, the advances in statistical mechanics and an increase of computer power have allowed the development of equations of state based on molecular principles that are accurate for real fluids and mixtures.

The most popular equation of state by using perturbation theory is the Statistical Associating Fluid Theory (SAFT) proposed by Chapman *et al.* (1988, 1990), who incorporated the thermodynamic perturbation theory (Wertheim, 1984a, 1984b, 1986a, 1986b, 1986c) with the equations of state that account for only physical interaction. The SAFT equations of state are based on the hypothesis that the residual Helmholtz energy

A^{res} of the fluid of interest is made up of three major contributions: the repulsion-dispersion contribution from monomeric segments, A^{seg}, the contribution from the formation of chains, A^{chain}, and the contribution from the formation of association complexes, A^{assoc}:

$$A^{res} = A^{seg} + A^{chain} + A^{assoc} \qquad (2.5.1)$$

As a result of this approach to account for the intermolecular forces involved, the SAFT equation can be applied to a wide variety of fluids which include systems involving alkanols, carboxylic acids and other industrially important mixtures. During the past eighteen years or so, a number of SAFT equations have been proposed by different researchers. The equation of state developed by Huang and Radosz (1990, 1991) has been the most widely used version of SAFT, which has been applicable to pure components and extended to correlate 60 phase equilibrium data sets for asymmetric and associating binary mixtures. Yu and Chen (1994) applied the SAFT equation to describe the LLE for 41 binary mixtures and 8 ternary mixtures with the pure component parameters obtained from Huang and Radosz (1990, 1991).

After the development of the original version of the SAFT equation by Chapman *et al.* (1990) and Huang and Radosz (1990), more effort has been made to modify the SAFT equations. Banaszak *et al.* (1993) extended the thermodynamic perturbation formalism to obtain one equation for the chain term of square-well statistical associating fluid theory (SW-SAFT). Ghonasgi and Chapman (1994) improved the SAFT equation by using the dimer fluid at the same volume fraction as the chain fluid to give a better estimate of the second virial coefficients. The second virial coefficients obtained were in better agreement with molecular simulation results at all densities and chain lengths than those of the original SAFT equation. Banaszak *et al.* (1994) developed an equation of state (LJ-SAFT) for Lennard-Jones chains by incorporating Lennard-Jones interactions into the thermodynamic perturbation theory. However, the results obtained for 8-mer, 16-mer, and 32-mer chains did not match the simulation data. Fu and Sandler (1995) simplified the SAFT equation by using a single attraction term of Lee *et al.* (1985) for the square-well fluid to replace the multiterm double series dispersive term to generate the Simplified SAFT equation of state (SSAFT). The SSAFT equation led to better VLE correlated results than the original SAFT equation while it was similar to or slightly

more accurate than the original SAFT equation in calculating pure component properties. Kraska and Gubbins (1996a, 1996b) proposed the Lennard-Jones SAFT equation (LJ-SAFT) where a Lennard-Jones equation was used to account for the segmental contribution instead of the BACK equation (Chen and Kreglewski, 1977) used in the original SAFT equation. The Lennard-Jones SAFT equation has been used to calculate the thermodynamic properties of pure fluids and binary mixtures. The calculated results for pure fluids shown in the phase diagram of the *n*-alkane, 1-alkanols and water obtained from LJ-SAFT equation were in better agreement with the experimental data than the original SAFT equation. Kraska and Gubbins (1996b) also applied the LJ-SAFT equation to describe the binary mixtures of *n*-alkane+*n*-alkane, 1-alkanol+*n*-alkane, and water+*n*-alkane with more accuracy than the SAFT equation. Subsequently, Galindo *et al.* (1996, 1997) proposed a simplified HS-SAFT equation that treats the molecules as chains of hard-sphere segments with van der-Waals interaction while the original SAFT equation treats the molecules as chains of Lennard-Jones segments. The HS-SAFT equation has been used to describe the critical behavior and phase equilibria of water+*n*-alkane (Galindo *et al.*, 1996) and water+hydofluoride (Galindo *et al.*, 1997) mixtures with good accuracy. Adidharma and Radosz (1999) applied six different square-well SAFT (SW-SAFT) models to predict the coexisting densities and second virial coefficients of pure *n*-alkanes. The performance of different models also was compared in their work. They concluded that the models resulting in low values of the segment energy and weak molecular weight dependence of the parameters were more accurate for real fluids.

2.6 The Cubic Plus Association (CPA) Equations of State

A special variant of the SAFT-type models was proposed by Kontogeorgis *et al.* (1996), who presented a new equation of state (Cubic-Plus-Association) for associating compounds. The Cubic-Plus-Association (CPA) equation combines the SRK EOS employed for the physical part and the theoretical background of the perturbation theory for the chemical part. The CPA EOS for pure compounds is given by

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} + \frac{RT}{V}\rho\sum_{A}\left(\frac{1}{X^{A}} - \frac{1}{2}\right)\frac{\partial X^{A}}{\partial \rho} \qquad (2.6.1)$$

where the mole fraction X^A of molecules not bonded at site A can be defined as

$$X^A = \left(1 + \rho \sum_B X^B \Delta^{AB}\right)^{-1} \tag{2.6.2}$$

The association strength Δ^{AB} is approximated by the following equation:

$$\Delta^{AB} = g(d)^{seg} \left[\exp(\varepsilon^{AB} / kT) - 1\right] \sigma^3 k^{AB} \tag{2.6.3}$$

where ε^{AB} is the association energy of interaction between sites A and B; k is the Boltzmann constant; k^{AB} is the volume of the interaction between sites A and B and the radial distribution function $g(d)^{seg}$ is defined as

$$g(d)^{seg} = \frac{2 - \eta}{2(1-\eta)^3} \tag{2.6.4}$$

The reduced fluid density, η, is expressed as a function of the temperature-dependent segment diameter, d, and the segment number, m:

$$\eta = \frac{\pi N_{AV}}{6} \rho m d^3 \tag{2.6.5}$$

The temperature-independent diameter, σ, is related to the soft core volume, v^*:

$$v^* = \frac{\pi N_{AV}}{6\tau} \sigma^3 \tag{2.6.6}$$

where N_{AV} is the Avogadro number and τ has the value of 0.74048.

The temperature-dependent segment diameter, d, is given by

$$\frac{d}{\sigma} = 1 - C \exp\left(\frac{-3u^0}{kT}\right) \tag{2.6.7}$$

where the well depth, u^0 / kT, is an energy parameter and C is the integration constant in the SAFT equation.

The CPA EOS has been used to produce good correlations of vapor pressures and saturated liquid volumes for primary-alcohols, phenol, tert-butyl alcohol, triethylene glycol and water. Later on, Voutsas *et al.* (1997) applied the CPA EOS to LLE calculations of alcohol+hydrocarbon mixtures. The performance of the CPA EOS has been compared with that of the Soave-RK (SRK) EOS (Soave, 1984), the UNIFAC model and the ESD EOS (Suresh and Elliott, 1992). They concluded that the CPA EOS gave better results than the SRK EOS and UNIFAC model and it was comparable to

those obtained from the ESD model. The CPA EOS also has been successfully used to describe the VLE and LLE of self-associating and cross-associating mixtures containing alcohols, glycols, water and hydrocarbons (Yakoumis *et al.*, 1998; Kontogeorgis *et al.*, 1999; Derawi *et al.*, 2003a, b). Recently, the CPA EOS has been extended to the modeling of organic acids (Derawi *et al.*, 2004) with excellent binary VLE and acceptable LLE correlations for acid+aliphatic hydrocarbon mixtures. Folas *et al.* (2005) applied the CPA EOS to VLE, LLE and SLE of alcohol+hydrocarbon and alcohol/glycol+water systems and to the multiphase equilbria of the acetic acid+water+hexane mixture with satisfactory results.

2.7 Lattice-Fluid Associated Solution Model (LFAS)

Panayiotou (Panayiotou, 1988; 1989; 1990) proposed an approximate statistical thermodynamic model called the Lattice-Fluid Associated Solution (LFAS) model to describe the thermodynamic behavior of pure alkanols and alkanol+*n*-alkane mixtures. Later on, Panayiotou and Sanchez (1991) incorporated the hydrogen bonding effect into a lattice model called the Sanchez-Lacombe EOS (Sanchez and Lacombe, 1976; Lacombe and Sanchez, 1976) to develop the Sanchez-Lacombe-Panayiotou (SLP) EOS. The SLP EOS is based on the assumption that the partition function is the product of two terms: a physical partition function due to the intermolecular interactions and an associating partition function which is used to take into account the hydrogen bonds in the system and calculated from the distribution of the hydrogen bonds among the proton-donor and acceptor groups of molecules. Panayiotou and Sanchez (1991) applied the SLP EOS to the calculations of three typical cases including self-associated solvents, polymer+solvent mixtures and polymer+polymer mixtures. In particular, The SLP EOS presented an advantage over the LFAS approach in extending its use to polymer mixtures and it was applicable to water-containing systems.

Although some thermodynamic models have been developed by means of chemical theory, perturbation theory, or lattice/quasi-chemical theory, the developed models are complex and involving relatively larger number of terms and parameters than most of the simple equations of state. Thus it is still desirable to modify simple equations of state with a view to extending their application to associating systems.

CHAPTER 3
DEVELOPMENT OF MODELS

A generic cubic equation of state has the following form:

$$P = \frac{n_T RT}{V - n_T \hat{b}} - \frac{n_T^2 \hat{a}}{(V + c_1 n_T \hat{b})(V + c_2 n_T \hat{b})} \tag{3.0}$$

where $\hat{a}$ and $\hat{b}$ are the equation of state parameters, which can be evaluated from the selected mixing rules; c_1 and c_2 are two distinct constants that determine the specific form of the equation of state; and n_T is the total number of moles in the system. The general forms of closed-form equations of state corresponding to the generic cubic equation of state for two association schemes and two selected mixing rules will be developed in this Chapter. In this regard, the expressions used to evaluate the parameters $\hat{a}$ and $\hat{b}$ will involve the term n_0, which is the total number of moles that would exist if there were no association.

Equation (3.0) is pressure-explicit and can be readily used to obtain the expressions for fugacity, enthalpy, entropy and other thermodynamic functions. However, the relationship between n_T and n_0 must be established first. The mixing rules chosen for evaluating the equation of state parameters and the association model selected for the chemical equilibrium are involved in deriving the expression of the ratio, n_T / n_0. The derivation of the equations for calculating the ratio, n_T / n_0 corresponding to two association schemes and two different mixing rules is presented in the following Section. The developed equations are first applied to a system consisting of only one associating species (i.e., species A) and any number of non-associating species, and then extended to the systems involving more than one associating species.

3.1 Heidemann-Prausnitz Approach to Defining Mixture Parameters

Heidemann and Prausnitz (1976) introduced the following reasonable simplifying assumptions that the energy parameter a is proportional to the square of the molecular size and the size parameter b may be taken as proportional to the molecular size. To facilitate the derivation of the closed-form equation of state, we recall the following equations presented in Chapter 2:

$$a_j = j^2 a_1 \tag{2.2.6}$$

$$b_j = j b_1 \tag{2.2.7}$$

where a_1 and b_1 are the monomer parameters, which in generally can be obtained from the critical properties of pure substances.

The conventional van der Waals-type mixing rules with an additional interaction parameter δ_{ij} between species i and j are given by

$$\hat{a} = \sum_i \sum_j z_i z_j (a_i a_j)^{0.5} (1 - \delta_{ij}) \tag{3.1.1}$$

$$\hat{b} = \sum_i z_i b_i \tag{2.2.9}$$

where z_i is the true mole fraction defined as $z_i = n_i / n_T$. It has been shown that the following equations (Heidemann and Prausnitz, 1976) can be obtained upon substituting Equations (2.2.6) and (2.2.7) into the conventional van der Waals-type mixing rules given in Equations (3.1.1) and (2.2.9):

$$\hat{a} = \left(\frac{n_0}{n_T}\right)^2 \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - \delta_{ij}) = \left(\frac{n_0}{n_T}\right)^2 \overline{a} \tag{3.1.2}$$

$$\hat{b} = \left(\frac{n_0}{n_T}\right) \sum_i x_i b_i = \left(\frac{n_0}{n_T}\right) \overline{b} \tag{3.1.3}$$

where $\hat{a}$ and $\hat{b}$ refer to the overall parameters of the associated solution; $\overline{a}$ and $\overline{b}$ stand for the parameters of the mixture; the indices i and j refer to all the species in a mixture as if there were no association. The reformulated equation can be obtained by inserting Equations (3.1.2) and (3.1.3) into Equation (3.0),

$$P = \frac{n_T RT}{V - n_0 \bar{b}} - \frac{n_0^2 \bar{a}}{(V + c_1 n_0 \bar{b})(V + c_2 n_0 \bar{b})} = \left(\frac{n_T}{n_0}\right)\frac{RT}{v - \bar{b}} - \frac{\bar{a}}{(v + c_1 \bar{b})(v + c_2 \bar{b})} \qquad (3.1.4)$$

where v is the apparent molar volume given by $v = V / n_0$. The fugacity coefficient $\hat{\phi}_i$ of the component i in a mixture can be calculated via the following equation:

$$\hat{\phi}_i = \exp\left\{\int_V^\infty \left[(RT)^{-1}\left(\partial P / \partial n_i\right)_{T,V,n_{j\neq i}} - 1/V\right] dV - \ln Z\right\} \qquad (3.1.5)$$

In the above expression, the partial derivative of pressure P with respect to n_i must be evaluated from the chosen equation of state. Upon substituting Equation (3.1.4) into Equation (3.1.5), one obtains the expressions for calculating the fugacity coefficients for the non-associating component k,

$$\hat{\phi}_k = \left(\frac{n_T}{n_0}\right)\left[\frac{RT}{P(v - \bar{b})}\right]\left(\frac{v + c_1 \bar{b}}{v + c_2 \bar{b}}\right)^{\frac{-\bar{a}\gamma_k}{(c_1 - c_2)\bar{b}RT}} \exp\left[\left(\frac{n_T}{n_0}\right)\left(\frac{b_k}{\bar{b}}\right)(Z - 1)\right] \qquad (3.1.6)$$

and that for the j-mer of the associating species A,

$$\hat{\phi}_{Aj} = \left(\frac{n_T}{n_0}\right)\left[\frac{RT}{P(v - \bar{b})}\right]\left(\frac{v + c_1 \bar{b}}{v + c_2 \bar{b}}\right)^{\frac{-j\bar{a}\gamma_{A1}}{(c_1 - c_2)\bar{b}RT}} \exp\left[j\left(\frac{n_T}{n_0}\right)\left(\frac{b_{A1}}{\bar{b}}\right)(Z - 1)\right] \qquad (3.1.7)$$

where γ_i can be expressed by the following equation:

$$\gamma_i = \frac{2\sum_p x_p (a_p a_i)^{0.5}(1 - \delta_{pi})}{\bar{a}} - \frac{b_i}{\bar{b}} \qquad (3.1.8)$$

and the true compressibility factor Z is defined as $Z = PV/(n_T RT)$.

Heidemann and Prausnitz (1976) made the simplifying assumption, which was originally proposed by Lassettre (1937) and Kempter and Mecke (1940), that the chemical equilibrium constant K_A is independent of the degree of association. The chemical equilibrium constant K_A is given by the following expression for pure associating species A:

$$K_A = \frac{\hat{\phi}_{A2} z_{A2}}{\hat{\phi}_{A1}^2 z_{A1}^2 P} = \frac{\hat{\phi}_{A3} z_{A3}}{\hat{\phi}_{A1}\hat{\phi}_{A2} z_{A1} z_{A2} P} = \ldots = \frac{\hat{\phi}_{A,j+1} z_{A,j+1}}{\hat{\phi}_{A1}\hat{\phi}_{Aj} z_{A1} z_{Aj} P} \qquad (3.1.9)$$

The authors also showed that the ratio $P\hat{\phi}_{A1}\hat{\phi}_{Aj} / \hat{\phi}_{A,j+1}$ in Equation (3.1.9) is independent of the index j and has a value dependent only upon the repulsive pressure

term of the equation of state. For convenience, the combined term, $P\hat{\phi}_{A1}\hat{\phi}_{Aj}/\hat{\phi}_{A,j+1}$ is designated as α, which is given by

$$\alpha = \frac{n_T}{n_0}\frac{RT}{(v-\bar{b})} \tag{3.1.10}$$

To evaluate the term, n_T/n_0 in Equation (3.1.4) and to solve for the true mole fraction of the monomer, z_{A1}, the following material balance equation is used:

$$\frac{n_{A0}}{n_T} = z_{A1} + 2z_{A2} + 3z_{A3} + ... + jz_{Aj} \tag{3.1.11}$$

where we take an infinite number of terms for infinite linear association and two terms for monomer-dimer association. The relationship between the mole fraction of the *j*-mer and that of the monomer is expressed as

$$z_{Aj} = (K_A\alpha)^{j-1} z_{A1}^j \tag{3.1.12}$$

3.1.1 Infinite Linear Association Model

Upon substituting Equation (3.1.12) into Equation (3.1.11), and using an infinite number of terms, one gets

$$\frac{n_{A0}}{n_T} = \sum_{j=1}^{\infty} j(K_A\alpha)^{j-1} z_{A1}^j \tag{3.1.1.1}$$

Using the two mathematical relations as follows for any real number *a*, $0 < a < 1$:

$$\sum_{i=1}^{\infty} a^i = \frac{a}{1-a} \tag{3.1.1.2}$$

$$\sum_{i=1}^{\infty} ia^i = \frac{a}{(1-a)^2} \tag{3.1.1.3}$$

Equation (3.1.1.1) can be expressed in the following form when *j* approaches to infinity:

$$\frac{n_{A0}}{n_T} = \frac{z_{A1}}{(1-K_A\alpha z_{A1})^2} \tag{3.1.1.4}$$

Multiplying both side of Equation (3.1.1.4) by n_A/n_{A0} leads to

$$\frac{n_A}{n_T} = \frac{n_A}{n_{A0}}\frac{z_{A1}}{(1-K_A\alpha z_{A1})^2} \tag{3.1.1.5}$$

The expression for the material balance is given below:

$$\frac{n_A}{n_T} = \sum_{j=1}^{\infty} z_{Aj} = \sum_{j=1}^{\infty} (K_A \alpha)^{j-1} z_{A1}^{j} = \frac{z_{A1}}{(1 - K_A \alpha z_{A1})} \tag{3.1.1.6}$$

Equation (3.1.1.6) can be rearranged to give

$$z_{A1} = \frac{n_A / n_T}{1 + K_A \alpha n_A / n_T} \tag{3.1.1.7}$$

A comparison of Equation (3.1.1.5) with Equation (3.1.1.6) gives

$$\frac{n_A}{n_{A0}} = 1 - K_A \alpha z_{A1} \tag{3.1.1.8}$$

Upon simplifying the resulting expression and after inserting Equation (3.1.10) and Equation (3.1.1.7) into Equation (3.1.1.8), one has

$$\frac{n_A}{n_{A0}} = \frac{1}{1 + \frac{K_A RT}{v - \bar{b}} \left(\frac{n_{A0}}{n_0} \right) \left(\frac{n_A}{n_{A0}} \right)} \tag{3.1.1.9}$$

The solution for the ratio n_A / n_{A0} is given by

$$\frac{n_A}{n_{A0}} = \frac{2}{1 + \sqrt{1 + \frac{4K_A RT}{v - \bar{b}} \left(\frac{n_{A0}}{n_0} \right)}} = \frac{2}{1 + \sqrt{1 + \frac{4K_A RTx_A}{v - \bar{b}}}} \tag{3.1.1.10}$$

where the apparent mole fraction of associating component A is defined as $x_A = n_{A0} / n_0$. Since the ratio of the true total mole number, n_T to the apparent total mole number, n_0 is given by

$$\frac{n_T}{n_0} = \frac{n_T - n_A}{n_0} + \frac{n_{A0}}{n_0} \frac{n_A}{n_{A0}} \tag{3.1.1.11}$$

substitution of Equation (3.1.1.10) into the above equation gives the expression:

$$\frac{n_T}{n_0} = \frac{n_0 - n_{A0}}{n_0} + \frac{n_{A0}}{n_0} \frac{n_A}{n_{A0}} = 1 - x_A \left(1 - \frac{2}{1 + \sqrt{1 + \frac{4K_A RTx_A}{v - \bar{b}}}} \right) \tag{3.1.1.12}$$

One may obtain the expression for calculating the true mole fraction of the monomer, z_{A1} from Equation (3.1.1.8) by referring to Equations (3.1.10), (3.1.1.10) and (3.1.1.12):

$$z_{A1} = \frac{2x_A}{1+\sqrt{1+\frac{4K_A RTx_A}{v-\bar{b}}}+\frac{2(1-x_A)x_A K_A RT}{v-\bar{b}}} \qquad (3.1.1.13)$$

Equation (3.1.1.12) is identical to Equation (25) presented by Wenzel and Krop (1990) in their paper. The ratio n_T / n_0 is unity when there is no association and approaches zero when there is complete association. Upon setting the value of x_A in Equation (3.1.1.12) equal to unity, we readily obtain the expression identical to Equation (19) given by Nan *et al.* (2001a) for a pure associating substance. The ratio n_T / n_0 and the true mole fraction of the monomer, z_{A1} have the same expression shown as follows:

$$\frac{n_T}{n_0} = z_{A1} = \frac{2}{1+\sqrt{1+\frac{4K_A RT}{v-\bar{b}}}} \qquad (3.1.1.14)$$

For mixtures containing more than one associating species, three types of chemical equilibria are involved in the derivation of the ratio n_T / n_0. The theoretical work is much more complex for these systems. For a binary mixture in which both component A and B can self-associate continuously to form linear polymers (dimers, trimers, etc.) like A_2, A_3,... and B_2, B_3,.... The general formula for the solvated species is A_iB_j. The solvation equilibria have the following form:

$$A_i + B_j \rightleftharpoons A_iB_j \qquad (3.1.1.15)$$

where the values of indexes i and j vary from 1 to infinity. The expression for the chemical equilibrium constant, K_A for component A has been given in Equation (3.1.9). A similar simplifying assumption and definition hold for component B and the solvated species A_iB_j. The equilibrium constant, K_B can be applied to all B_j equilibria and K_{AB} for all solvation equilibria as

$$K_B = \frac{\hat{\phi}_{B2} z_{B2}}{\hat{\phi}_{B1}^2 z_{B1}^2 P} = \frac{\hat{\phi}_{B3} z_{B3}}{\hat{\phi}_{B1}\hat{\phi}_{B2} z_{B1} z_{B2} P} = \ldots = \frac{\hat{\phi}_{B,j+1} z_{B,j+1}}{\hat{\phi}_{B1}\hat{\phi}_{Bj} z_{B1} z_{Bj} P} \qquad (3.1.1.16)$$

and

$$K_{AB} = \frac{\hat{\phi}_{A_iB_j} z_{A_iB_j}}{\hat{\phi}_{A_i}\hat{\phi}_{B_j} z_{A_i} z_{B_j} P} \qquad (3.1.1.17)$$

By referring to the approach described by Ikonomou and Donohue (1988), one has the following material balance equations:

$$\sum_{i=1}^{\infty} z_{Ai} + \sum_{j=1}^{\infty} z_{Bj} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} C_{ij} z_{A_iB_j} = 1 \qquad (3.1.1.18)$$

$$x_A \frac{n_0}{n_T} = \sum_{i=1}^{\infty} i z_{Ai} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i C_{ij} z_{A_iB_j} \qquad (3.1.1.19)$$

$$x_B \frac{n_0}{n_T} = \sum_{j=1}^{\infty} j z_{Bj} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j C_{ij} z_{A_iB_j} \qquad (3.1.1.20)$$

where the binomial coefficient C_{ij} is defined in $C_{ij} = (i+j)!/(i!\,j!)$. As the combined term $P\hat{\phi}_{A1}\hat{\phi}_{Aj}/\hat{\phi}_{A,j+1}$ is designated as α_A in Equation (3.1.10), similar definitions hold for component B and cross-association species AB. Therefore,

$$\alpha_A = \alpha_B = \alpha_{AB} = \frac{n_T}{n_0}\frac{RT}{(v-\bar{b})} \qquad (3.1.1.21)$$

The relationship between the mole fraction of the *j*-mer and that of the monomer is given by the following equations for component A, B and AB, respectively:

$$z_{Aj} = (K_A\alpha_A)^{j-1} z_{A1}^{j} \qquad (3.1.1.22)$$

$$z_{Bj} = (K_B\alpha_B)^{j-1} z_{B1}^{j} \qquad (3.1.1.23)$$

$$z_{A_iB_j} = K_{AB}\alpha_{AB}(K_A\alpha_A)^{i-1} z_{A1}^{i} (K_B\alpha_B)^{j-1} z_{B1}^{j} \qquad (3.1.1.24)$$

Substitution of Equations (3.1.1.21 - 3.1.1.24) into Equation (3.1.1.18) and multiplying Equation (3.1.1.18) by n_T/n_0 leads to

$$\frac{n_T}{n_0} = \sum_{i=1}^{\infty}\frac{(v-\bar{b})}{K_A RT}\left[\frac{K_A RT}{(v-\bar{b})}\frac{n_T}{n_0} z_{A1}\right]^{i} + \sum_{j=1}^{\infty}\frac{(v-\bar{b})}{K_B RT}\left[\frac{K_B RT}{(v-\bar{b})}\frac{n_T}{n_0} z_{B1}\right]^{j}$$
$$+ \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} C_{ij}\frac{K_{AB}(v-\bar{b})}{K_A K_B RT}\left[\frac{K_A RT}{(v-\bar{b})}\frac{n_T}{n_0} z_{A1}\right]^{i}\left[\frac{K_B RT}{(v-\bar{b})}\frac{n_T}{n_0} z_{B1}\right]^{j} \qquad (3.1.1.25)$$

Upon using the relations in Equations (3.1.1.2) and (3.1.1.3) to simplify Equation (3.1.1.25), one may obtain

$$\frac{n_T}{n_0} = \frac{S_A}{1-R_A S_A} + \frac{S_B}{1-R_B S_B} + \frac{R_{AB}}{R_A R_B}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} C_{ij}(R_A S_A)^{i}(R_B S_B)^{j} \qquad (3.1.1.26)$$

where

$$R_A = \frac{K_A RT}{(v-\bar{b})} \tag{3.1.1.27}$$

$$R_B = \frac{K_B RT}{(v-\bar{b})} \tag{3.1.1.28}$$

$$R_{AB} = \frac{K_{AB} RT}{(v-\bar{b})} \tag{3.1.1.29}$$

$$S_A = \frac{n_T z_{A1}}{n_0} = \frac{n_{A1}}{n_0} \tag{3.1.1.30}$$

$$S_B = \frac{n_T z_{B1}}{n_0} = \frac{n_{B1}}{n_0} \tag{3.1.1.31}$$

Substitution of Equations (3.1.1.21 - 3.1.1.24) into Equations (3.1.1.19) and (3.1.1.20) leads to

$$x_A \frac{n_0}{n_T} = \sum_{i=1}^{\infty} i \left[\frac{K_A RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{i-1} z_{A1}^i + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} iC_{ij} \frac{K_{AB} RT}{(v-\bar{b})} \frac{n_T}{n_0} \left[\frac{K_A RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{i-1} z_{A1}^i \left[\frac{K_B RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{j-1} z_{B1}^j \tag{3.1.1.32}$$

$$x_B \frac{n_0}{n_T} = \sum_{j=1}^{\infty} j \left[\frac{K_B RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{j-1} z_{B1}^j + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} jC_{ij} \frac{K_{AB} RT}{(v-\bar{b})} \frac{n_T}{n_0} \left[\frac{K_A RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{i-1} z_{A1}^i \left[\frac{K_B RT}{(v-\bar{b})} \frac{n_T}{n_0} \right]^{j-1} z_{B1}^j \tag{3.1.1.33}$$

Upon simplifying the above equations, one gets

$$x_A = \frac{S_A}{(1-R_A S_A)^2} + \frac{R_{AB}}{R_A R_B} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} iC_{ij} (R_A S_A)^i (R_B S_B)^j \tag{3.1.1.34}$$

$$x_B = \frac{S_B}{(1-R_B S_B)^2} + \frac{R_{AB}}{R_A R_B} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} jC_{ij} (R_A S_A)^i (R_B S_B)^j \tag{3.1.1.35}$$

There are three unknowns S_A, S_B and n_T / n_0 in Equations (3.1.1.26), (3.1.1.34) and (3.1.1.35). S_A and S_B can be solved from Equations (3.1.1.34) and (3.1.1.35), simultaneously, and then the mole ratio n_T / n_0 can be obtained directly from Equation (3.1.1.26) by substituting the values of S_A and S_B into Equation (3.1.1.26). The

following approximate analytical equations which are not mathematically rigorous, can be obtained by referring to the approach proposed by Ikonomou and Donohue (1988) when the cross-association constant K_{AB} is taken as $K_{AB} = \sqrt{K_A K_B}$.

$$S_A = \frac{4x_A}{\left(1+\sqrt{1+\frac{4K_A RT}{v-\bar{b}}}\right)^2} \tag{3.1.1.36}$$

$$S_B = \frac{4x_B}{\left(1+\sqrt{1+\frac{4K_B RT}{v-\bar{b}}}\right)^2} \tag{3.1.1.37}$$

$$\frac{n_T}{n_0} = \frac{2x_A}{1+\sqrt{1+\frac{4K_A RT}{v-\bar{b}}}} + \frac{2x_B}{1+\sqrt{1+\frac{4K_B RT}{v-\bar{b}}}} \tag{3.1.1.38}$$

The above analytical method and conclusions can be extended to mixtures involving more than one associating component (i.e., m associating species and n non-associating species). In such a case, the analytical solution for the mole ratio n_T / n_0 is given by

$$\frac{n_T}{n_0} = \sum_{i=1}^{m} \frac{2x_i}{1+\sqrt{1+\frac{4K_i RT}{v-\bar{b}}}} + \sum_{j=m+1}^{m+n} x_j \tag{3.1.1.39}$$

It can be seen that Equation (3.1.1.39) is not consistent with Equation (3.1.1.12) upon setting the number of associating species m equal to 1. Therefore the following equation is proposed for multicomponent systems containing m associating species and n non-associating species in which the number of associating species m can be taken as 1. This proposal is largely based on the analysis presented by Anderko (1989d) and Nan *et al.* (2001b). As a result, the following equation is consistent with Equation (3.1.1.12):

$$\frac{n_T}{n_0} = \sum_{i=1}^{m} \frac{2x_i}{1+\sqrt{1+\frac{4K_i RT\sum_{j=1}^{m} x_j}{v-\bar{b}}}} + \sum_{j=m+1}^{m+n} x_j \tag{3.1.1.40}$$

3.1.2 Monomer-dimer Association Model

The degree of association j in Equation (3.1.11) is 2 for monomer-dimer association, and Equation (3.1.11) can be simplified to

$$\frac{n_{A0}}{n_T} = z_{A1} + 2z_{A2} \tag{3.1.2.1}$$

Substitution of Equation (3.1.12) into Equation (3.1.2.1) leads to

$$\frac{n_{A0}}{n_T} = z_{A1} + 2K_A \alpha z_{A1}^2 \tag{3.1.2.2}$$

The material balance equation is written as

$$\frac{n_A}{n_T} = z_{A1} + z_{A2} = z_{A1} + K_A \alpha z_{A1}^2 = \frac{n_A n_{A0}}{n_{A0} n_T} = \frac{n_A n_0 x_A}{n_{A0} n_T} \tag{3.1.2.3}$$

An expression for the mole fraction of the monomer can be readily obtained from Equation (3.1.2.3):

$$z_{A1} = \frac{-1 + \sqrt{1 + 4K_A \alpha \dfrac{n_A}{n_T}}}{2K_A \alpha} \tag{3.1.2.4}$$

and one has

$$\frac{n_A}{n_{A0}} = \frac{n_A / n_T}{n_{A0} / n_T} \tag{3.1.2.5}$$

Substitution of Equations (3.1.2.2 - 3.1.2.4) into Equation (3.1.2.5) leads to

$$\frac{n_A}{n_{A0}} \left\{ \frac{-1 + \sqrt{1 + 4K_A \alpha \dfrac{n_A}{n_T}}}{2K_A \alpha} + 2K_A \alpha \left[\frac{-1 + \sqrt{1 + 4K_A \alpha \dfrac{n_A}{n_T}}}{2K_A \alpha} \right]^2 \right\} = \frac{n_A}{n_T} \tag{3.1.2.6}$$

Upon substituting Equation (3.1.10) into the above equation and rearranging it, one obtains

$$1 + \frac{4K_A RT}{v - \bar{b}} \frac{n_A}{n_{A0}} x_A - \sqrt{1 + \frac{4K_A RT}{v - \bar{b}} \frac{n_A}{n_{A0}} x_A} - \frac{2x_A K_A RT}{v - \bar{b}} = 0 \tag{3.1.2.7}$$

An appropriate solution to this pseudo-quadratic equation is

$$\sqrt{1 + \frac{4K_A RT}{v - \bar{b}} \frac{n_A}{n_{A0}} x_A} = \frac{1 + \sqrt{1 + \dfrac{8K_A RT x_A}{v - \bar{b}}}}{2} \tag{3.1.2.8}$$

and the expression for the ratio n_A / n_{A0} is

$$\frac{n_A}{n_{A0}} = \frac{1}{2} + \frac{1}{1+\sqrt{1+\frac{8K_A RTx_A}{v-\bar{b}}}} \tag{3.1.2.9}$$

Substitution of Equation (3.1.2.9) into Equation (3.1.1.11) results in the following expression:

$$\frac{n_T}{n_0} = (1-x_A) + x_A\left(\frac{1}{2} + \frac{1}{1+\sqrt{1+\frac{8K_A RTx_A}{v-\bar{b}}}}\right) \tag{3.1.2.10}$$

The desired equation can be obtained upon simplifying Equation (3.1.2.10):

$$\frac{n_T}{n_0} = 1 - x_A\left(\frac{1}{2} - \frac{1}{1+\sqrt{1+\frac{8K_A RTx_A}{v-\bar{b}}}}\right) \tag{3.1.2.11}$$

which is the same as Equation (55) given by Nan *et al.* (2001a) in their paper. Upon simplifying the resulting expression after inserting Equations (3.1.2.5), (3.1.2.11) and (3.1.10) into Equation (3.1.2.9), one obtains the corresponding expression for calculating the true mole fraction of the monomer:

$$z_{A1} = \frac{4}{2 + x_A + (2-x_A)\sqrt{1+\frac{8K_A RTx_A}{v-\bar{b}}}} \tag{3.1.2.12}$$

The resulting equations for the mole ratio and mole fraction of monomer of a pure associating substance can be obtained by setting the value of x_A in Equations (3.1.2.11) and (3.1.2.12) equal to unity. The simplified expressions are identical to Equation (20) given by Nan *et al.* (2001a) for a pure associating substance as shown below:

$$\frac{n_T}{n_0} = \frac{1}{2} + \frac{1}{1+\sqrt{1+\frac{8K_A RT}{v-\bar{b}}}} \tag{3.1.2.13}$$

$$z_{A1} = \frac{4}{3+\sqrt{1+\frac{8K_A RT}{v-\bar{b}}}} \tag{3.1.2.14}$$

The monomer-dimer association model can be applied to binary mixtures with more than one associating species. For the simplest case in which both components A and B are associating species, only the cross-association species AB is considered in addition to the species A_1, B_1, A_2 and B_2. The chemical equilibrium is represented by the following reaction for the cross-association species AB:

$$A_1 + B_1 \rightleftharpoons AB \tag{3.1.2.15}$$

and the equilibrium constant for the cross-association reaction is defined as follows:

$$K_{AB} = \frac{\hat{\phi}_{AB} z_{AB}}{\hat{\phi}_{A1} z_{A1} \hat{\phi}_{B1} z_{B1} P} \tag{3.1.2.16}$$

To solve for the mole ratio n_T / n_0, one needs the following material balance and chemical equilibrium equations:

$$z_{A1} + z_{A2} + z_{B1} + z_{B2} + z_{AB} = 1 \tag{3.1.2.17}$$

$$\frac{n_0}{n_T} x_A = z_{A1} + 2z_{A2} + z_{AB} \tag{3.1.2.18}$$

$$\frac{n_0}{n_T} x_B = z_{B1} + 2z_{B2} + z_{AB} \tag{3.1.2.19}$$

$$K_A = \frac{1}{\alpha} \frac{z_{A2}}{z_{A1}^2} \tag{3.1.2.20}$$

$$K_B = \frac{1}{\alpha} \frac{z_{B2}}{z_{B1}^2} \tag{3.1.2.21}$$

$$K_{AB} = \frac{1}{\alpha} \frac{z_{AB}}{z_{A1} z_{B1}} \tag{3.1.2.22}$$

where the combined term α is given in Equation (3.1.10).

Comparison of Equations (3.1.2.18) and (3.1.2.19) with Equation (3.1.2.17) leads to

$$\frac{n_0}{n_T} = 2 - z_{A1} - z_{B1} \tag{3.1.2.23}$$

Upon substituting Equations (3.1.2.20), (3.1.2.22), (3.1.2.23) and (3.1.10) into Equation (3.1.2.18), one obtains

$$z_{A1}=\frac{-\left[1+\frac{2K_{AB}RT}{(v-\bar{b})}\frac{n_T}{n_0}-\frac{K_{AB}RT}{(v-\bar{b})}\right]+\sqrt{\left[1+\frac{2K_{AB}RT}{(v-\bar{b})}\frac{n_T}{n_0}-\frac{K_{AB}RT}{(v-\bar{b})}\right]^2+\frac{4(2K_A-K_{AB})RTx_A}{(v-\bar{b})}}}{\frac{2(2K_A-K_{AB})RT}{(v-\bar{b})}\frac{n_T}{n_0}} \tag{3.1.2.24}$$

Similarly, one gets

$$z_{B1}=\frac{-\left[1+\frac{2K_{AB}RT}{(v-\bar{b})}\frac{n_T}{n_0}-\frac{K_{AB}RT}{(v-\bar{b})}\right]+\sqrt{\left[1+\frac{2K_{AB}RT}{(v-\bar{b})}\frac{n_T}{n_0}-\frac{K_{AB}RT}{(v-\bar{b})}\right]^2+\frac{4(2K_B-K_{AB})RTx_B}{(v-\bar{b})}}}{\frac{2(2K_B-K_{AB})RT}{(v-\bar{b})}\frac{n_T}{n_0}} \tag{3.1.2.25}$$

There are three unknowns, which are z_{A1}, z_{B1} and n_T/n_0 in non-linear Equations (3.1.2.23 - 3.1.2.25). The procedure for solving three unknowns will involve the following steps: 1). Choosing the initial value of n_T/n_0 first, and then solving Equations (3.1.2.24) and (3.1.2.25) for z_{A1} and z_{B1}. 2). Recalculating n_T/n_0 by means of Equation (3.1.2.23), then using the new value of n_T/n_0 to get the new values of z_{A1} and z_{B1}. 3). The iteration will be proceeding until the condition that the change of n_T/n_0 is less than the tolerance is met.

3.2 Hu et al. Approach to Defining Mixture Parameters

Hu *et al.* (1984) suggested a generalized formula for relating the energy parameter of an associating system to replace Equation (3.1.2). The formula is

$$\hat{a}=(n_0/n_T)^{1+w}\,\bar{a} \tag{3.2.1}$$

where $0\le w\le 1$. The authors used the above equation mainly because the experimental values of the energy parameters for normal alkanes, calculated on the basis of Equation (2.2.6), tend to overestimate the effect of the degree of association on the energy parameter. Hu and his coworkers (Hu *et al.*, 1984; Hong and Hu, 1989; Zhao and Hu, 1990) have used a value of zero for w in all their studies. Upon setting w equal to zero and substituting Equations (3.2.1) and (3.1.3) into Equation (3.0), one obtains another closed-form equation of state for associating systems:

$$P = \frac{n_T RT}{V - n_0 \bar{b}} - \frac{n_T n_0 \bar{a}}{(V + c_1 n_0 \bar{b})(V + c_2 n_0 \bar{b})} = \left(\frac{n_T}{n_0}\right)\left[\frac{RT}{v - \bar{b}} - \frac{\bar{a}}{(v + c_1 \bar{b})(v + c_2 \bar{b})}\right] \quad (3.2.2)$$

The fugacity coefficient equations corresponding to Equation (3.2.2) can be derived using the classical thermodynamic relation, Equation (3.1.5). The resulting equation for the non-associating component k has the form:

$$\hat{\phi}_k = \left(\frac{n_T}{n_0}\right)\left[\frac{RT}{P(v - \bar{b})}\right]\left(\frac{v + c_1 \bar{b}}{v + c_2 \bar{b}}\right)^{\frac{-\bar{a} n_T / n_0 (\gamma_k - 1)}{(c_1 - c_2)\bar{b} RT}} \exp\left[(\frac{n_T}{n_0})(\frac{b_k}{\bar{b}})(Z - 1)\right] \quad (3.2.3)$$

and that for the j-mer of the associating species A has the form:

$$\hat{\phi}_{Aj} = \left(\frac{n_T}{n_0}\right)\left[\frac{RT}{P(v - \bar{b})}\right]\left(\frac{v + c_1 \bar{b}}{v + c_2 \bar{b}}\right)^{\frac{-\bar{a}[1 + j n_T / n_0 (\gamma_{A1} - 1)]}{(c_1 - c_2)\bar{b} RT}} \exp\left[j(\frac{n_T}{n_0})(\frac{b_{A1}}{\bar{b}})(Z - 1)\right] \quad (3.2.4)$$

where the expression for γ_i is given in Equation (3.1.8).

As the approach of Hu et al. rather than of Heidemann-Prausnitz is used to define mixture parameters, the final form of the closed-form equation of state has been changed from Equation (3.1.4) to Equation (3.2.2). As a result, the value of the combined term $P\hat{\phi}_{A1}\hat{\phi}_{Aj} / \hat{\phi}_{A,j+1}$ in Equation (3.1.9), corresponding to Equation (3.1.4), is changed to

$$\alpha = \frac{n_T}{n_0} \frac{\beta RT}{(v - \bar{b})} \quad (3.2.5)$$

where β represents the group of term and is given by the following equation:

$$\beta = \left(\frac{v + c_1 \bar{b}}{v + c_2 \bar{b}}\right)^{\frac{-\bar{a}}{(c_1 - c_2)\bar{b} RT}} \quad (3.2.6)$$

3.2.1 Infinite Linear Association Model

Following the same procedure as the one used in the previous Section, one can derive the equations for calculating the mole ratio n_T / n_0 in Equation (3.2.2) and the mole fraction of the monomer, z_{A1} from both material balance equations and equilibrium relations. The resulting expressions are more complex than Equations (3.1.1.12) and (3.1.1.13) due to the different forms of the combined term $P\hat{\phi}_{A1}\hat{\phi}_{Aj} / \hat{\phi}_{A,j+1}$, as shown in Equations (3.1.10) and (3.2.5), and they are given by

$$\frac{n_T}{n_0} = 1 - x_A \left(1 - \frac{2}{1 + \sqrt{1 + \frac{4\beta K_A RT x_A}{v - \bar{b}}}} \right) \tag{3.2.1.1}$$

and

$$z_{A1} = \frac{2x_A}{1 + \sqrt{1 + \frac{4\beta K_A RT x_A}{v - \bar{b}}} + \frac{2(1 - x_A) x_A \beta K_A RT}{v - \bar{b}}} \tag{3.2.1.2}$$

The expression for the mole ratio n_T / n_0 and mole fraction of monomer, z_{A1} are also applicable to a pure associating substance by setting the value of x_A equal to unity. The resulting expression is

$$\frac{n_T}{n_0} = z_{A1} = \frac{2}{1 + \sqrt{1 + \frac{4\beta K_A RT}{v - \bar{b}}}} \tag{3.2.1.3}$$

For multicomponent systems containing m associating species and n non-associating species, one obtains the following expression by following the same procedure as shown in Section 3.1.1:

$$\frac{n_T}{n_0} = \sum_{i=1}^{m} \frac{2x_i}{1 + \sqrt{1 + \frac{4\beta K_i RT \sum_{j=1}^{m} x_j}{v - \bar{b}}}} + \sum_{j=m+1}^{m+n} x_j \tag{3.2.1.4}$$

3.2.2 Monomer-dimer Association Model

The monomer-dimer association model can be used to obtain the mole ratio n_T / n_0 in Equation (3.2.2) and the mole fraction of the monomer, z_{A1} which are expressed in the following equations, respectively:

$$\frac{n_T}{n_0} = 1 - x_A \left(\frac{1}{2} - \frac{1}{1 + \sqrt{1 + \frac{8\beta K_A RT x_A}{v - \bar{b}}}} \right) \tag{3.2.2.1}$$

and

$$z_{A1} = \frac{4}{2 + x_A + (2 - x_A)\sqrt{1 + \dfrac{8\beta K_A RT x_A}{v - \bar{b}}}} \tag{3.2.2.2}$$

The above two equations work for the generic equation of state with $c_1 = c_2$ except that the β term that corresponds to Equation (3.2.6) is given by

$$\beta = \exp\left[\frac{-\bar{a}}{RT(v - \bar{b})}\right] \tag{3.2.2.3}$$

Upon setting x_A equal to unity, the expressions for the mole ratio and mole fraction of monomer given in Equations (3.2.2.1) and (3.2.2.2) can be simplified to give

$$\frac{n_T}{n_0} = \frac{1}{2} + \frac{1}{1 + \sqrt{1 + \dfrac{8\beta K_A RT}{v - \bar{b}}}} \tag{3.2.2.4}$$

and

$$z_{A1} = \frac{4}{3 + \sqrt{1 + \dfrac{8\beta K_A RT}{v - \bar{b}}}} \tag{3.2.2.5}$$

for pure associating species.

As described in Section 3.1.2, the monomer-dimer association model can be applied to binary mixtures in which both components are associating species. One can obtain the mole ratio n_T / n_0 by solving Equation (3.1.2.23) and the following equations, simultaneously. The solution method is similar to the one presented in Section 3.1.2.

$$z_{A1} = \frac{-\left[1 + \dfrac{2\beta K_{AB} RT}{(v - \bar{b})}\dfrac{n_T}{n_0} - \dfrac{\beta K_{AB} RT}{(v - \bar{b})}\right] + \sqrt{\left[1 + \dfrac{2\beta K_{AB} RT}{(v - \bar{b})}\dfrac{n_T}{n_0} - \dfrac{\beta K_{AB} RT}{(v - \bar{b})}\right]^2 + \dfrac{4(2K_A - K_{AB})\beta RT x_A}{(v - \bar{b})}}}{\dfrac{2(2K_A - K_{AB})\beta RT}{(v - \bar{b})}\dfrac{n_T}{n_0}} \tag{3.2.2.6}$$

$$z_{B1} = \frac{-\left[1 + \dfrac{2\beta K_{AB} RT}{(v - \bar{b})}\dfrac{n_T}{n_0} - \dfrac{\beta K_{AB} RT}{(v - \bar{b})}\right] + \sqrt{\left[1 + \dfrac{2\beta K_{AB} RT}{(v - \bar{b})}\dfrac{n_T}{n_0} - \dfrac{\beta K_{AB} RT}{(v - \bar{b})}\right]^2 + \dfrac{4(2K_B - K_{AB})\beta RT x_B}{(v - \bar{b})}}}{\dfrac{2(2K_B - K_{AB})\beta RT}{(v - \bar{b})}\dfrac{n_T}{n_0}} \tag{3.2.2.7}$$

3.3 Reformulated Peng-Robinson Equations of State

The Peng-Robinson (Peng and Robinson, 1976) equation of state is a special case of the generic equation shown in Equation (3.0) with $c_1 = 1+\sqrt{2}$ and $c_2 = 1-\sqrt{2}$. By incorporating an infinite linear or a monomer-dimer association model into the Peng-Robinson equation and adopting two different sets of mixing rules suggested by Heidemann and Prausnitz (1976), and Hu *et al.* (1984), respectively, the reformulated Peng-Robinson equations of state have been developed. For clarity, the equations are outlined as follows:

1. Model PPR-1, which is based on infinite linear association, with the mixing rules proposed by Hu *et al.* (1984).

   a. For a pure associating component A,

$$P = \left(\frac{2}{1+\sqrt{1+\dfrac{4\beta K_A RT}{v-\bar{b}}}} \right) \left\{ \frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \right\} \qquad (3.3.1.a)$$

where $\bar{a}$ and $\bar{b}$ are identical to the monomer parameters a and b. Equation (3.3.1.a) can be simplified to

$$P = \left(\frac{2}{1+\sqrt{1+\dfrac{4\beta K_A RT}{v-b}}} \right) \left\{ \frac{RT}{v-b} - \frac{a}{[v+(1+\sqrt{2})b][v+(1-\sqrt{2})b]} \right\} \qquad (3.3.1.b)$$

   b. For mixtures involving only one associating component A,

$$P = \left\{ 1-x_A \left(1 - \frac{2}{1+\sqrt{1+\dfrac{4\beta K_A RT x_A}{v-\bar{b}}}} \right) \right\} \left\{ \frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \right\} \qquad (3.3.2)$$

   c. For mixtures involving *m* associating species where *m* > *1* and *n* non-associating species,

$$P=\left(\sum_{i=1}^{m}\frac{2x_i}{1+\sqrt{1+\frac{4\beta K_i RT\sum_{j=1}^{m}x_j}{v-\bar{b}}}}+\sum_{j=m+1}^{m+n}x_j\right)\left\{\frac{RT}{v-\bar{b}}-\frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]}\right\}$$

(3.3.3)

2. Model PPR-2, which is based on monomer-dimer association, with the mixing rules proposed by Hu *et al.* (1984).

   a. For a pure associating component A,

$$P=\left(\frac{1}{2}+\frac{1}{1+\sqrt{1+\frac{8\beta K_A RT}{v-\bar{b}}}}\right)\left\{\frac{RT}{v-\bar{b}}-\frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]}\right\} \qquad (3.3.4.a)$$

which can be expressed in another form

$$P=\left(\frac{1}{2}+\frac{1}{1+\sqrt{1+\frac{8\beta K_A RT}{v-b}}}\right)\left\{\frac{RT}{v-b}-\frac{a}{[v+(1+\sqrt{2})b][v+(1-\sqrt{2})b]}\right\} \qquad (3.3.4.b)$$

   b. For mixtures involving only one associating component A,

$$P=\left\{1-x_A\left[\frac{1}{2}-\frac{1}{1+\sqrt{1+\frac{8\beta K_A RTx_A}{v-\bar{b}}}}\right]\right\}\left\{\frac{RT}{v-\bar{b}}-\frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]}\right\}$$

(3.3.5)

   c. For binary mixtures involving two associating species, the mole ratio n_T / n_0 can be obtained by solving Equations (3.1.2.23), (3.2.2.6) and (3.2.2.7).

The value of β in Equations (3.3.1 - 3.3.5) is calculated from Equation (3.2.6) with $c_1 = 1+\sqrt{2}$ and $c_2 = 1-\sqrt{2}$.

3. Model PPR-3, which is based on infinite linear association, with the mixing rules proposed by Heidemann and Prausnitz (1976).

   a. For a pure associating component A,

$$P = \frac{2}{1+\sqrt{1+\frac{4K_A RT}{v-\bar{b}}}}\frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \tag{3.3.6.a}$$

which can be expressed in another form

$$P = \frac{2}{1+\sqrt{1+\frac{4K_A RT}{v-b}}}\frac{RT}{v-b} - \frac{a}{[v+(1+\sqrt{2})b][v+(1-\sqrt{2})b]} \tag{3.3.6.b}$$

   b. For mixtures involving only one associating component A,

$$P = \left(1-x_A+\frac{2x_A}{1+\sqrt{1+\frac{4K_A RTx_A}{v-\bar{b}}}}\right)\frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \tag{3.3.7}$$

   c. For mixtures involving m associating species where $m > 1$ and n non-associating species,

$$P = \left(\sum_{i=1}^{m}\frac{2x_i}{1+\sqrt{1+\frac{4K_i RT\sum_{j=1}^{m}x_j}{v-\bar{b}}}}+\sum_{j=m+1}^{m+n}x_j\right)\frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \tag{3.3.8}$$

4. Model PPR-4, which is based on monomer-dimer association, with the mixing rules proposed by Heidemann and Prausnitz (1976).

   a. For a pure associating component A,

$$P = \left(\frac{1}{2}+\frac{1}{1+\sqrt{1+\frac{8K_A RT}{v-\bar{b}}}}\right)\frac{RT}{v-\bar{b}} - \frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]} \tag{3.3.9.a}$$

which can be expressed in another form

$$P=\left(\frac{1}{2}+\frac{1}{1+\sqrt{1+\frac{8K_A RT}{v-b}}}\right)\frac{RT}{v-b}-\frac{a}{[v+(1+\sqrt{2})b][v+(1-\sqrt{2})b]} \qquad (3.3.9.b)$$

b. For mixtures involving only one associating component A,

$$P=\left\{1-x_A\left[\frac{1}{2}-\frac{1}{1+\sqrt{1+\frac{8K_A RTx_A}{v-\bar{b}}}}\right]\right\}\frac{RT}{v-\bar{b}}-\frac{\bar{a}}{[v+(1+\sqrt{2})\bar{b}][v+(1-\sqrt{2})\bar{b}]}$$

(3.3.10)

c. For binary mixtures involving two associating species, the mole ratio n_T / n_0 can be obtained by solving Equations (3.1.2.23 - 3.1.2.25).

CHAPTER 4
DATA REDUCTION FOR PURE SUBSTANCES

The reformulated Peng-Robinson equations presented in Equations (3.3.1.b), (3.3.4.b), (3.3.6.b) and (3.3.9.b) have been used to correlate the vapor pressures and liquid densities of pure associating substances. In each of the equations mentioned above, three parameters are required to represent each pure component. The parameters are the physical parameters a and b, and the chemical parameter K. As proposed by the previous authors (Hu *et al.*, 1984; Ikonomou and Donohue, 1986; Anderko, 1992), these three parameters are simultaneously determined by fitting the reformulated equations to the experimental vapor pressure and liquid density data of pure substances. Although the associating substances consist of monomer, dimer and etc., the monomer is the only independent species. The parameters presented in the reformulated equations can be treated in the same manner as in the conventional equation of state. Initially, the parameters a and b take the values of the original PR EOS and then the parameter K is evaluated. Next, by increasing or decreasing a, b and repeating the regression until a minimum in the sum of squares of the vapor pressure and liquid density errors between the experimental data and the calculated results is achieved.

To facilitate the calculation, both the energy parameter a and the equilibrium constant K are treated as functions of temperature and the size parameter b as a constant for all forms of reformulated equations except Equation (3.3.6.b) in which the size parameter b can be expressed as a function of temperature as well. The temperature-dependent parameters can be well represented by the following equations for Model PPR-1,

$$a/\left(\text{bar m}^6\text{mol}^{-2}\right)=\left(a_{11}+a_{12}\sqrt{T/\text{K}}\right)^2 \tag{4.1}$$

for Model PPR-2,

$$a/\left(\text{bar m}^6\text{mol}^{-2}\right)=\left(a_{21}+a_{22}\sqrt{T/\text{K}}\right)^2 \tag{4.2}$$

for Model PPR-3,

$$a/\left(\text{bar m}^6\text{mol}^{-2}\right) = a_{31} + a_{32}\sqrt{T/\text{K}} + a_{33}\left(T/\text{K}\right) \tag{4.3}$$

$$b/\left(\text{m}^3\text{mol}^{-1}\right) = \left(b_{31} + b_{32}\sqrt{T/K}\right)^2 \tag{4.4}$$

and for Model PPR-4,

$$a/\left(\text{bar m}^6\text{mol}^{-2}\right) = a_{41} + a_{42}\sqrt{T/\text{K}} + a_{43}\left(T/\text{K}\right) \tag{4.5}$$

The chemical equilibrium constant K is taken to be a function of temperature and to have the same form for the four models, i.e.:

$$\ln(K/\text{bar}^{-1}) = E_1/(T/\text{K}) + E_2 \tag{4.6}$$

It should be noted that even setting the size parameter b as functions of temperature, there is no obvious improvement on the correlations of vapor pressure and liquid density of pure associating compounds for Models PPR-1, PPR-2 and PPR-4.

Tables 4.1 - 4.4 list the coefficients in Equations (4.1 - 4.6) and the optimal values of b determined for pure associating substances in the reformulated equations The experimental data sources used to determine the parameter values are also indicated in the tables for each substance. The values of the chemical association constant K, calculated with the given coefficients is consistent with setting the standard pressure equal to one bar. All calculations are based on using bar as the unit of pressure.

The vapor pressure and liquid density values calculated by means of the reformulated equations are presented in Tables 4.5 - 4.9. The FORTRAN programs for the four models are attached in Appendix B. The calculated results have been compared with the experimental data reported in the literature and with the corresponding values reported by Hong and Hu (1989) and Nan *et al.* (2001a) to assess the quality of the representations. It should be noted that Hong and Hu (1989) did not list the data sources for selected polar substances. The root-mean-square (RMS) values they presented for associating substances appear to be the overall deviations of the calculated results. Table 4.5 lists the RMS values from four reformulated equations and the Hong-Hu equation (Hong and Hu, 1989) for selected alkanols, water and polar substances for comparison. It can be seen that in general Model PPR-3 is capable of representing both vapor pressures and liquid densities of associating substances with better accuracy than Models PPR-1, PPR-2, PPR-4 and the Hong-Hu equation. The temperature ranges of the

experimental data and the RMS values of the calculated vapor pressures and liquid densities obtained from Models PPR-2, PPR-4 and the Hong-Hu equation for selected acids are presented in Tables 4.6 and 4.7 for comparison. The data serves to show that both Models PPR-2 and PPR-4 are clearly superior to the Hong-Hu equation in the representation of the vapor pressures of acids. On the other hand, Model PPR-2 and the Hong-Hu equation give comparable results for the correlation of liquid densities of acids whereas the correlation obtained from Model PPR-4 is seen to be not as good.

The capabilities of the four reformulated equations to represent the vapor pressures and liquid densities of associating substances are also compared with those of the AMH equation (Nan *et al.*, 2001a). The comparisons of the vapor pressure and liquid density data, which are expressed in average absolute percentage deviation (AAPD), are shown in Tables 4.8 and 4.9, respectively. It should be pointed out that the origin of the data used by Nan *et al.* (2001a) is different from the one used in this study. It appears that Nan *et al.* (2001a) used smoothing function-generated values reported in the compilation by Smith and Srivastava (1986) instead of the original experimental values to determine the values of the parameters. It can be seen that the reformulated equations are capable of correlating the vapor pressures more accurately than the AMH equation, with the exception of Model PPR-1, while the reformulated equations, with the exception of Model PPR-4, perform better than the AMH equation in the correlation of the liquid densities of associating substances. The AMH equation involves more adjustable parameters than the other equations but this flexibility does not necessarily result in better representation of thermodynamic properties.

As the reformulated equations are used to represent the phase behavior of associating mixtures involving hydrocarbons in the next Chapter, it is necessary to determine the equation of state parameters for the hydrocarbons. Table 4.10 lists the equation of state parameters for a number of hydrocarbons as well as the AAPD values of the calculated vapor pressures and liquid densities obtained from this work and the RMS values of those calculated from the Hong-Hu equation. It can be seen that the PR EOS can be used to accurately represent the liquid densities of hydrocarbons over a wide temperature range by using the parameters determined from both vapor pressure and liquid density values taken from the data compilation of Smith and Srivastava (1986).

Table 4.1: Values of Parameters in Model PPR-1 to Represent Alkanols and Water

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^3\ a_{11}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1}$	$10^6\ a_{12}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1} \cdot K^{-1/2}$	E_1/K	E_2	Reference
Water	15.70	3.3869	-1.8239	4200	-13.89	Vukalovich et al. (1969)
Methanol	35.10	4.8898	-3.6865	3937	-16.31	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Ethanol	49.70	6.3046	-5.7093	3127	-11.43	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
1-Propanol	65.90	7.3736	-6.3363	3050	-11.68	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Propanol	65.30	7.2006	-6.4748	2962	-12.36	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
1-Butanol	81.50	8.3415	-6.7621	3100	-13.58	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Butanol	80.40	8.0580	-6.8246	3160	-14.84	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
Isobutanol	78.50	7.8803	-6.2037	2855	-14.23	Ambrose and Sprake (1970); Ambrose and Townsend (1963)
Tert-butanol	82.50	8.0896	-7.5027	2836	-14.56	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales et al. (1983)
Pentanol	97.50	9.4897	-7.6842	2800	-14.33	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Hexanol	115.00	10.7477	-8.8308	2600	-14.16	Garg et al. (1993); Kemme and Kreps (1969)
Heptanol	131.00	11.8571	-9.7197	2500	-14.31	Garg et al. (1993); Kemme and Kreps (1969)
Octanol	148.00	12.5011	-9.3866	2430	-14.26	Ambrose and Sprake (1970); Hales and Ellender (1976)
Decanol	185.60	14.4136	-10.1702	2300	-14.01	Costello and Bowden (1958a); Kemme and Kreps (1969)
Dodecanol	222.00	15.9293	-10.2414	2255	-14.08	Ambrose and Sprake (1970); Hales and Ellender (1976)

Table 4.2: Values of Parameters in Model PPR-2 to Represent Associating Substances

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^3\ a_{21}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1}$	$10^3\ a_{22}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1} \cdot K^{-1/2}$	E_1/K	E_2	Reference
Water	15.68	4.1233	-0.0739	4100	-13.08	Vukalovich et al. (1969)
Methanol	34.50	6.1282	-0.1418	5115	-15.05	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Ethanol	50.20	8.0840	-0.2019	4982	-15.87	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
1-Propanol	65.80	9.7478	-0.2453	3560	-13.50	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Propanol	66.50	9.6446	-0.2495	2900	-13.35	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
1-Butanol	82.00	11.1384	-0.2747	3150	-13.35	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Butanol	81.00	10.7977	-0.2731	3050	-14.07	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
Isobutanol	79.60	10.5610	-0.2567	2900	-14.05	Ambrose and Sprake (1970); Ambrose and Townsend (1963)
Tert-butanol	82.10	10.7959	-0.2857	2802	-14.08	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales et al. (1983)
Pentanol	97.85	12.5590	-0.3069	2750	-14.03	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Hexanol	114.35	14.1010	-0.3454	2586	-14.08	Garg et al. (1993); Kemme and Kreps (1969)
Heptanol	131.00	15.6660	-0.3851	2456	-14.04	Garg et al. (1993); Kemme and Kreps (1969)
Octanol	148.00	16.4635	-0.3859	2366	-14.01	Ambrose and Sprake (1970); Hales and Ellender (1976)
Decanol	185.90	18.9853	-0.4311	2301	-13.88	Costello and Bowden (1958a); Kemme and Kreps (1969)
Dodecanol	223.20	21.0675	-0.4579	2252	-14.06	Ambrose and Sprake (1970); Hales and Ellender (1976)

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^3\ a_{21}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1}$	$10^3\ a_{22}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1} \cdot K^{-1/2}$	E_1/K	E_2	Reference
Formic acid	33.40	4.9375	-0.0643	6425	-17.36	Coolidge (1928); Timmermans (1965); Ambrose and Ghiassee (1987)
Acetic acid	51.48	7.0360	-0.1253	7237	-18.67	Ambrose et al. (1977); Hales et al. (1983)
Acrylic acid	62.59	9.1430	-0.2022	7931	-17.24	Daubert and Danner (1989)
Propionic acid	67.80	9.4640	-0.2057	7486	-17.80	Hales et al. (1983); Ambrose et al. (1981)
Butyric acid	85.88	11.4230	-0.2539	7602	-18.98	Ambrose et al. (1981); Costello and Bowden (1958b)
Isobutyric acid	86.75	11.4150	-0.2545	6213	-20.02	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Pentanoic acid	103.59	13.4180	-0.3047	8278	-21.45	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Isovaleric acid	103.69	13.1480	-0.2986	7823	-21.21	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Hexanoic acid	134.98	16.3400	-0.3862	8460	-22.02	Ambrose et al. (1981); Costello and Bowden (1958b)
Octanoic acid	156.30	18.3000	-0.4218	9125	-23.53	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Acetone	62.00	7.0710	-0.1368	2865	-13.95	Ambrose et al. (1974); Felsing and Durban (1926)
Nitromethane	48.40	6.6330	-0.1133	3245	-13.48	Daubert and Danner (1989)
Formaldehyde	30.20	4.1850	-0.0838	3196	-13.26	Daubert and Danner (1989)
Acetaldehyde	45.00	5.6130	-0.1157	3960	-13.11	Smith and Bonner (1951)
Propionaldehyde	60.64	6.9070	-0.1359	3057	-13.26	Smith and Bonner (1951)
Methyl chloride	39.30	4.5180	-0.0862	3021	-13.01	Daubert and Danner (1989)
Methylene chloride	52.60	6.2200	-0.1186	3570	-13.43	Daubert and Danner (1989)
Chloroform	66.40	7.1480	-0.1346	4225	-13.87	Campbell and Chatterjee (1968)

Table 4.3: Values of Parameters in Model PPR-3 to Represent Alkanols and Water

Substance	$10^6\ a_{31}$ bar·m^6·mol^{-2}	$10^6\ a_{32}$ bar·m^6·mol^{-2}·K$^{-1/2}$	$10^6\ a_{33}$ bar·m^6·mol^{-2}·K^{-1}	$10^3\ b_{31}$ m$^{3/2}$·mol$^{-1/2}$	$10^6\ b_{32}$ m$^{3/2}$·mol$^{-1/2}$·K$^{-1/2}$	E_1/K	E_2	Reference
Water	8.0545	-0.4277	0.0113	0.0998	1.9805	3000	-12.25	Vukalovich et al. (1969)
Methanol	15.7791	-1.0845	0.0262	0.1206	4.6745	3000	-11.25	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Ethanol	36.4459	-2.6531	0.0654	0.1590	4.8161	3000	-11.85	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
1-Propanol	75.2718	-5.8163	0.1402	0.2016	4.2789	3000	-11.95	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Propanol	70.7593	-5.6572	0.1413	0.1888	5.1473	3000	-12.15	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
1-Butanol	93.9992	-6.6046	0.1550	0.2381	3.9467	3000	-12.35	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Butanol	96.2892	-7.5099	0.1883	0.2170	5.0935	3000	-12.45	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
Isobutanol	103.2669	-7.5449	0.1759	0.2710	2.3412	3000	-12.45	Ambrose and Sprake (1970); Ambrose and Townsend (1963)

Substance	$10^6\ a_{31}$ $bar \cdot m^6 \cdot mol^{-2}$	$10^6\ a_{32}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1/2}$	$10^6\ a_{33}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1}$	$10^3\ b_{31}$ $m^{3/2} \cdot mol^{-1/2}$	$10^6\ b_{32}$ $m^{3/2} \cdot mol^{-1/2} \cdot K^{-1/2}$	E_1/K	E_2	Reference
Tert-butanol	104.4756	-8.9526	0.2350	0.1909	6.7867	3000	-12.45	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales et al. (1983)
Pentanol	120.9149	-8.3299	0.1966	0.2464	4.8735	3000	-12.45	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Hexanol	120.0669	-6.8836	0.1505	0.2702	4.9022	3000	-12.45	Garg et al. (1993); Kemme and Kreps (1969)
Heptanol	188.6226	-12.3641	0.2810	0.2827	5.4811	3000	-12.45	Garg et al. (1993); Kemme and Kreps (1969)
Octanol	119.3561	-3.5615	0.0445	0.3275	4.3436	3000	-12.45	Ambrose and Sprake (1970); Hales and Ellender (1976)
Decanol	332.1366	-19.6899	0.3897	0.3967	2.9836	3000	-12.45	Costello and Bowden (1958a); Kemme and Kreps (1969)
Dodecanol	175.0677	0.5265	-0.1444	0.4890	0.5002	3000	-12.45	Ambrose and Sprake (1970); Hales and Ellender (1976)

Table 4.4: Values of Parameters in Model PPR-4 to Represent Associating Substances

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^6\ a_{41}$ $bar \cdot m^6 \cdot mol^{-2}$	$10^6\ a_{42}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1/2}$	$10^6\ a_{43}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1}$	E_1/K	E_2	Reference
Water	16.90	11.8041	-0.5120	0.0078	4034	-13.25	Vukalovich et al. (1969)
Methanol	35.40	16.7282	-0.6709	0.0074	5087	-14.98	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Ethanol	52.90	41.6893	-2.5055	0.0485	4904	-15.73	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
1-Propanol	70.10	99.5269	-6.7330	0.0701	3490	-13.27	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Propanol	71.80	94.6978	-6.0431	0.1129	2890	-13.18	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
1-Butanol	87.50	135.4252	-8.6427	0.1631	3093	-13.25	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
2-Butanol	87.20	126.2542	-8.1013	0.1552	3032	-13.97	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales and Ellender (1976)
Isobutanol	86.30	114.8263	-6.5444	0.1107	2902	-14.07	Ambrose and Sprake (1970); Ambrose and Townsend (1963)

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^6\ a_{41}$ $bar \cdot m^6 \cdot mol^{-2}$	$10^6\ a_{42}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1/2}$	$10^6\ a_{43}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1}$	E_1/K	E_2	Reference
Tert-butanol	88.40	132.6511	-8.9758	0.1791	2826	-14.05	Ambrose and Sprake (1970); Ambrose and Townsend (1963); Hales et al. (1983)
Pentanol	104.30	156.8605	-8.5656	0.1366	2765	-14.03	Ambrose and Sprake (1970); Ambrose et al. (1975); Hales and Ellender (1976)
Hexanol	119.70	185.5720	-9.3482	0.1313	2550	-14.01	Garg et al. (1993); Kemme and Kreps (1969)
Heptanol	136.10	259.2070	-14.4282	0.2313	2450	-14.05	Garg et al. (1993); Kemme and Kreps (1969)
Octanol	151.40	315.6791	-17.6791	0.2843	2334	-13.96	Ambrose and Sprake (1970); Hales and Ellender (1976)
Decanol	188.40	487.3277	-29.0447	0.4997	2289	-13.77	Costello and Bowden (1958a); Kemme and Kreps (1969)
Dodecanol	226.00	579.0016	-31.9266	0.5033	2267	-13.53	Ambrose and Sprake (1970); Hales and Ellender (1976)
Formic acid	33.60	20.3393	-1.3111	0.0328	6534	-16.95	Coolidge (1928); Timmermans (1965); Ambrose and Ghiassee (1987)
Acetic acid	64.10	54.8677	-3.3817	0.0675	7675	-17.86	Ambrose et al. (1977); Hales et al. (1983)
Acrylic acid	62.60	37.7504	-1.3968	0.0077	7104	-11.95	Daubert and Danner (1989)

Substance	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^6\ a_{41}$ $bar \cdot m^6 \cdot mol^{-2}$	$10^6\ a_{42}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1/2}$	$10^6\ a_{43}$ $bar \cdot m^6 \cdot mol^{-2} \cdot K^{-1}$	E_1/K	E_2	Reference
Propionic acid	69.00	66.8021	-4.3943	0.0916	7380	-17.50	Hales et al. (1983); Ambrose et al. (1981)
Butyric acid	87.30	106.9257	-7.5379	0.1684	7501	-18.75	Ambrose et al. (1981); Costello and Bowden (1958b)
Isobutyric acid	94.00	99.8032	-6.4713	0.1494	6524	-19.23	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Pentanoic acid	108.00	116.0868	-7.3251	0.1582	8152	-20.23	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Isovaleric acid	110.50	121.0528	-7.8303	0.1819	7581	-20.94	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Hexanoic acid	128.40	128.7570	-6.8607	0.1458	8123	-21.96	Ambrose et al. (1981); Costello and Bowden (1958b)
Octanoic acid	169.00	182.5020	-9.4265	0.1980	8987	-23.23	Costello and Bowden (1958b); Ambrose and Ghiassee (1987)
Acetone	65.50	21.5850	0.0738	-0.0150	2843	-13.87	Ambrose et al. (1974); Felsing and Durban (1926)
Nitromethane	52.80	33.0238	-1.2489	0.0196	3104	-12.88	Daubert and Danner (1989)
Formaldehyde	31.30	9.2474	-0.4543	0.0095	3525	-13.47	Daubert and Danner (1989)
Acetaldehyde	46.00	0.1382	1.1634	-0.0431	3824	-13.08	Smith and Bonner (1951)
Propionaldehyde	63.90	0.2497	2.1814	-0.0756	3024	-13.14	Smith and Bonner (1951)
Methyl chloride	42.30	13.0914	-0.7504	0.0199	3025	-13.22	Daubert and Danner (1989)
Methylene chloride	56.70	30.2788	-1.9146	0.0481	3641	-13.85	Daubert and Danner (1989)
Chloroform	70.40	35.4824	-2.1075	0.0500	4234	-13.95	Campbell and Chatterjee (1968)

Table 4.5: Comparison of the Capabilities of the Five Different Models to Represent the Combined Vapor Pressures and Liquid Densities of Associating Substances

Substance	$N(P^{sat})^1$	$N(v^L)^2$	PPR-1	PPR-2	PPR-3	PPR-4	Hong and Hu (1989)	
			RMS %*	RMS %	RMS %	RMS %	T range/K	RMS %
Water	31	31	3.01	1.67	1.06	1.49	293-513	0.40
Methanol	25	8	0.19	0.79	0.28	0.46	293-393	0.78
Ethanol	41	10	1.41	0.95	0.35	1.19	293-473	0.67
1-Propanol	36	9	1.67	0.95	0.56	1.37	293-453	0.53
2-Propanol	33	9	1.87	1.05	0.38	0.96	293-433	0.60
1-Butanol	27	11	1.62	0.95	0.75	1.32	303-463	1.20
2-Butanol	20	10	1.76	0.94	0.52	1.14	313-393	0.81
Isobutanol	19	6	1.77	1.23	0.70	1.68	313-413	1.40
Tert-butanol	19	8	1.21	0.66	0.36	0.73	303-363	0.64
Pentanol	21	14	1.71	1.09	0.84	2.12	333-413	0.88
Hexanol	11	10	1.49	0.79	0.53	0.32	343-463	0.40
Heptanol	10	10	1.03	0.66	0.32	0.50	373-473	0.85
Octanol	15	14	1.30	1.04	1.02	1.26	363-423	1.20
Decanol	8	9	1.43	1.09	1.16	0.40	n.a.	n.a.
Dodecanol	19	5	1.36	0.90	0.38	0.40	n.a.	n.a.
Acetone	47	11	n.a.	0.48	n.a.	1.26	273-453	0.28
Nitromethane	21	21	n.a.	1.50	n.a.	3.05	293-473	0.31
Formaldehyde	19	19	n.a.	1.09	n.a.	2.85	213-413	0.38
Acetaldehyde	5	4	n.a.	0.44	n.a.	0.34	233-413	0.59
Propionaldehyde	10	5	n.a.	0.30	n.a.	0.64	253-453	0.61

Substance	N(P^{sat})	N(v^L)	PPR-1	PPR-2	PPR-3	PPR-4	Hong and Hu (1989)	
			RMS %*	RMS %	RMS %	RMS %	T range/K	T range/K
Methyl chloride	17	17	n.a.	2.64	n.a.	1.16	213-413	0.86
Methylene chloride	19	19	n.a.	1.80	n.a.	2.04	253-433	0.36
Chloroform	18	18	n.a.	1.68	n.a.	1.28	283-453	0.67
Average RMS %			1.52	1.07	0.61	1.22		0.69

[1]—Number of experimental vapor pressure data

[2]—Number of experimental liquid density data

$$* RMS\% = 100 \times \sqrt{\frac{\sum_{i=1}^{N(P^{sat})} \left(\frac{P_{cal,i} - P_{exp,i}}{P_{exp,i}} \right)^2 + \sum_{i=1}^{N(v^L)} \left(\frac{v_{exp,i} - v_{cal,i}}{v_{cal,i}} \right)^2}{N(P^{sat}) + N(v^L)}}$$

n.a.--not available

Table 4.6: Comparison of the Capabilities of the Three Different Models to Represent the Vapor Pressures of Selected Acids

Substance	T range/K	N	PPR-2	PPR-4	Hong and Hu (1989)	
			RMS %*	RMS %	T range/K	RMS %
Formic acid	273-393	32	0.68	0.26	293-473	0.69
Acetic acid	304-415	27	0.66	0.58	293-573	0.79
Acrylic acid	293-513	23	1.08	1.17	343-593	1.23
Propionic acid	328-438	28	0.40	0.29	293-573	1.40
Butyric acid	350-452	26	0.43	0.10	293-593	0.67
Isobutyric acid	344-446	27	0.08	0.37	333-573	1.18
Pentanoic acid	373-465	16	0.33	0.67	353-593	1.22
Isovaleric acid	364-456	20	0.27	0.07	333-593	0.99
Hexanoic acid	386-442	13	0.11	0.26	363-603	0.72
Octanoic acid	417-513	18	0.92	0.24	n.a.	n.a.
Average RMS %			0.50	0.40		0.99

$$* RMS\% = 100 \times \sqrt{\frac{\sum_{i=1}^{N(P^{sat})} \left[\left(P_{cal,i} - P_{\exp,i}\right)/ P_{\exp,i}\right]^2}{N(P^{sat})}}$$

Table 4.7: Comparison of the Capabilities of the Three Different Models to Represent the Liquid Densities of Selected Acids

Substance	T range/K	N	PPR-2	PPR-4	Hong and Hu (1989)	
			RMS %*	RMS %	T range/K	RMS %
Formic acid	273-298	3	1.46	1.85	293-433	1.60
Acetic acid	293-490	14	0.94	3.88	293-553	0.92
Acrylic acid	293-513	23	1.61	2.19	323-543	1.15
Propionic acid	288-490	15	1.46	2.16	293-533	0.95
Butyric acid	273-533	10	0.89	2.98	293-513	0.79
Isobutyric acid	333-513	10	0.71	3.30	333-553	0.74
Pentanoic acid	273-533	11	0.99	3.15	293-533	1.10
Isovaleric acid	333-513	10	0.67	3.00	333-553	0.78
Hexanoic acid	353-513	9	0.85	2.52	363-503	1.24
Octanoic acid	293-573	10	0.9	2.57	n.a.	n.a.
Average RMS %			1.05	2.76		1.03

$$* RMS\% = 100 \times \sqrt{\frac{\sum_{i=1}^{N(v^L)} \left[\left(v_{\exp,i} - v_{cal,i}\right)/ v_{cal,i}\right]^2}{N(v^L)}}$$

Table 4.8: Comparison of the Capabilities of the Five Different Models to Represent the Vapor Pressures of Associating Substances

Substance	T range/K	N	PPR-1	PPR-2	PPR-3	PPR-4	Nan et al. (2001a)	
			AAPD*	AAPD	AAPD	AAPD	T range/K	AAPD
Water	273-573	31	2.98	0.84	0.63	0.59	273-643	0.63
Methanol	288-393	25	0.13	0.68	0.17	0.13	273-493	1.72
Ethanol	293-514	41	0.95	0.48	0.29	0.27	273-503	0.98
1-Propanol	333-473	36	1.48	0.70	0.40	0.47	293-523	0.91
2-Propanol	325-490	33	1.65	0.79	0.20	0.20	278-450	0.65
1-Butanol	352-473	27	1.63	0.74	0.28	0.26	295-447	1.80
2-Butanol	341-474	20	1.82	0.93	0.42	0.29	281-488	0.69
Isobutanol	343-474	19	1.25	0.92	0.23	0.15	300-465	0.92
Tert-butanol	330-399	19	1.26	0.66	0.36	0.19	304-443	1.47
Pentanol	348-514	21	1.66	0.86	0.22	0.25	278-450	3.15
Hexanol	341-430	11	1.73	0.90	0.59	0.40	310-428	2.49
Heptanol	349-450	10	1.20	0.58	0.27	0.21	343-445	0.29
Octanol	386-554	15	1.16	0.79	0.50	0.12	338-549	0.62
Decanol	409-488	8	1.47	1.00	0.43	0.20	327-509	0.73
Dodecanol	446-550	19	1.32	0.84	0.24	0.19	n.a.	n.a.
Formic acid	273-393	32	n.a.	0.53	n.a.	0.19	299-392	0.84
Acetic acid	304-415	27	n.a.	0.55	n.a.	0.40	304-415	1.39
Acrylic acid	293-513	23	n.a.	0.87	n.a.	1.01	323-593	1.79
Propionic acid	328-438	28	n.a.	0.92	n.a.	0.21	328-438	0.57

Substance	T range/K	N	PPR-1	PPR-2	PPR-3	PPR-4	Nan et al. (2001a)	
			AAPD*	AAPD	AAPD	AAPD	T range/K	AAPD
Butyric acid	350-452	26	n.a.	0.37	n.a.	0.09	298-452	0.94
Isobutyric acid	344-446	27	n.a.	0.29	n.a.	0.31	n.a.	n.a.
Pentanoic acid	373-465	16	n.a.	0.07	n.a.	0.57	372-465	0.30
Isovaleric acid	364-456	20	n.a.	0.24	n.a.	0.06	n.a.	n.a.
Hexanoic acid	386-442	13	n.a.	0.09	n.a.	0.24	n.a.	n.a.
Octanoic acid	417-513	18	n.a.	0.79	n.a.	0.19	n.a.	n.a.
Acetone	259-508	47	n.a.	0.22	n.a.	1.01	263-478	1.53
Nitromethane	273-473	21	n.a.	0.32	n.a.	0.59	n.a.	n.a.
Formaldehyde	213-393	19	n.a.	0.61	n.a.	0.55	n.a.	n.a.
Acetaldehyde	273-294	5	n.a.	0.17	n.a.	0.35	n.a.	n.a.
Propionaldehyde	291-322	10	n.a.	0.27	n.a.	0.53	n.a.	n.a.
Methyl chloride	213-373	17	n.a.	0.89	n.a.	0.35	n.a.	n.a.
Methylene chloride	253-433	19	n.a.	1.65	n.a.	0.68	n.a.	n.a.
Chloroform	283-453	18	n.a.	1.05	n.a.	0.34	266-431	1.13
Average AAPD			1.45	0.65	0.35	0.35		1.16

$$* AAPD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{P_{cal,i} - P_{\exp,i}}{P_{\exp,i}}\right|$$

Table 4.9: Comparison of the Capabilities of the Five Different Models to Represent the Liquid Densities of Associating Substances

Substance	T range/K	N	PPR-1	PPR-2	PPR-3	PPR-4	Nan et al. (2001a)	
			AAPD*	AAPD	AAPD	AAPD	T range/K	AAPD
Water	273-573	31	1.81	1.72	1.16	1.76	273-643	4.37
Methanol	293-440	8	0.22	0.73	0.21	0.21	273-493	3.68
Ethanol	293-455	10	2.10	1.42	0.23	0.94	273-503	2.40
1-Propanol	293-480	9	0.49	0.55	0.79	1.39	293-523	1.46
2-Propanol	298-430	9	1.67	0.93	0.58	1.02	278-450	2.06
1-Butanol	293-490	11	0.56	0.67	1.00	1.36	295-447	2.03
2-Butanol	293-490	10	0.81	0.43	0.50	1.21	281-488	1.74
Isobutanol	421-477	6	1.98	1.28	0.65	1.01	300-465	1.84
Tert-butanol	301-400	8	0.56	0.28	0.20	0.89	304-443	1.51
Pentanol	293-490	14	0.96	0.81	0.86	1.32	278-450	1.92
Hexanol	323-373	10	0.54	0.20	0.20	0.29	310-428	1.72
Heptanol	323-373	10	0.29	0.25	0.32	0.28	343-445	1.65
Octanol	293-490	14	1.09	1.06	1.08	1.08	338-549	2.67
Decanol	393-553	9	0.83	0.84	1.04	0.38	327-509	4.86
Dodecanol	440-490	5	0.44	0.50	0.51	0.41	n.a.	n.a.
Formic acid	273-298	3	n.a.	1.42	n.a.	1.81	293-553	3.55
Acetic acid	293-490	14	n.a.	0.64	n.a.	3.10	293-583	3.44
Acrylic acid	293-513	23	n.a.	1.07	n.a.	1.90	323-593	3.53
Propionic acid	288-490	15	n.a.	0.83	n.a.	1.93	323-593	0.67
Butyric acid	273-533	10	n.a.	1.35	n.a.	2.45	343-563	3.22

Substance	T range/K	N	PPR-1	PPR-2	PPR-3	PPR-4	Nan et al. (2001a)	
			AAPD*	AAPD	AAPD	AAPD	T range/K	AAPD
Isobutyric acid	333-513	10	n.a.	0.53	n.a.	2.76	n.a.	n.a.
Pentanoic acid	273-533	11	n.a.	1.30	n.a.	2.74	353-623	1.05
Isovaleric acid	333-513	10	n.a.	0.49	n.a.	2.61	n.a.	n.a.
Hexanoic acid	353-513	9	n.a.	0.66	n.a.	2.14	n.a.	n.a.
Octanoic acid	293-573	10	n.a.	0.68	n.a.	1.77	n.a.	n.a.
Acetone	256-325	11	n.a.	0.79	n.a.	1.29	n.a.	n.a.
Nitromethane	273-473	21	n.a.	1.82	n.a.	3.65	n.a.	n.a.
Formaldehyde	213-393	19	n.a.	0.96	n.a.	3.37	n.a.	n.a.
Acetaldehyde	273-293	4	n.a.	0.07	n.a.	0.29	n.a.	n.a.
Propionaldehyde	273-303	5	n.a.	0.18	n.a.	0.53	n.a.	n.a.
Methyl chloride	213-373	17	n.a.	2.65	n.a.	1.28	n.a.	n.a.
Methylene chloride	253-433	19	n.a.	1.02	n.a.	2.39	n.a.	n.a.
Chloroform	283-453	18	n.a.	1.56	n.a.	1.56	n.a.	n.a.
Average AAPD			0.96	0.90	0.62	1.55		2.47

$$* AAPD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{v_{\exp,i} - v_{cal,i}}{v_{cal,i}}\right|$$

Table 4.10: Values of Parameters Used to Calculate Properties and Deviations (APPD) with Experimental Results for Selected Non-associating Substances

Substance	This Work						Hong and Hu (1989)	
	$10^6\ b$ $m^3 \cdot mol^{-1}$	$10^3\ a_{11}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1}$	$10^3\ a_{12}$ $bar^{1/2} \cdot m^3 \cdot mol^{-1} \cdot K^{-1/2}$	t/°C	AAPD(P^{sat})	AAPD($1/v^L$)	t/°C	RMS %
n-Butane	75.0	6.680	-0.1341	-60-120	1.47	2.56	-60-120	0.35
n-Pentane	92.3	8.120	-0.1637	-20-140	0.84	1.29	-20-140	0.18
Isohexane	107.6	9.098	-0.1758	0-160	0.65	0.80	0-180	0.25
n-Hexane	108.5	9.353	-0.1840	0-180	0.61	1.12	0-180	0.40
2-Methylhexane	126.0	10.631	-0.2139	20-200	0.48	1.23	20-200	0.34
n-Heptane	126.4	10.865	-0.2185	20-200	0.52	0.69	20-200	0.40
n-Octane	144.0	12.424	-0.2558	40-220	0.34	0.68	40-220	0.45
n-Nonane	162.3	13.953	-0.2908	60-240	0.34	0.58	60-240	0.30
n-Decane	179.0	15.421	-0.3246	80-260	0.29	0.83	80-260	0.41
Cyclohexane	91.8	8.507	-0.1514	20-180	0.55	0.78	20-180	0.56
Benzene	76.3	7.880	-0.1412	30-150	0.39	0.27	30-150	0.41
Toluene	93.2	9.195	-0.1649	40-220	0.47	0.56	40-220	0.33
Ethylbenzene	109.8	10.543	-0.1932	40-220	0.52	0.40	40-220	0.45
m-Xylene	110.0	10.619	-0.1948	60-240	0.22	0.45	60-240	0.15
o-Xylene	108.6	10.590	-0.1913	60-240	0.41	0.37	60-240	0.45
p-Xylene	110.4	10.475	-0.1875	60-240	0.44	0.53	60-240	0.18

Data Source: Smith and Srivastava (1986)

CHAPTER 5
VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

Vapor-liquid equilibrium (VLE) has been widely used in industrial separation processes. The basic principle of a VLE calculation is that the fugacities of each species are equal in both phases:

$$f_i^L(T,P,x) = f_i^V(T,P,y) \tag{5.0.1}$$

where f_i is the fugacity of component i in a mixture. The superscripts V and L denote vapor phase and liquid phase, respectively. If an activity coefficient or excess Gibbs free energy model is used to describe the liquid phase and an equation of state model is applied to the fugacity calculation in the vapor phase, then we define this as the γ-ϕ method, and Equation (5.0.1) becomes

$$f_i^L(T,P,x) = P_i^{sat}(T)x_i\gamma_i(T,P,x)\exp\left[\int_{P^{sat}}^{P}\frac{v}{RT}dP\right] = f_i^V(T,P,y) = Py_i\hat{\phi}_i^V(T,P,y) \tag{5.0.2}$$

The Poynting Correction Factor $\exp\left[\int_{P^{sat}}^{P}\frac{v}{RT}dP\right]$ in Equation (5.0.2) would be used to correct for pressures away from the saturation pressures. An alternative method is to use an equation of state for both phases. The basic equilibrium relation then becomes

$$f_i^L(T,P,x) = Px_i\hat{\phi}_i^L(T,P,x) = f_i^V(T,P,y) = Py_i\hat{\phi}_i^V(T,P,y) \tag{5.0.3}$$

The VLE description using an equation of state for both phases is referred to as the $\phi-\phi$ method. This method is relatively complex to apply in comparison with the γ-ϕ method. However, it can be applied to the predictions or correlations of various properties such as density, enthalpy and etc., while the γ-ϕ method can only be used to describe the VLE at low and moderate pressures.

The most commonly encountered types of VLE calculations are bubble-point, dew-point and flash. They are classified into the following categories:

- Bubble-point pressure calculations: compute $\{y_i\}$ and P at specified $\{x_i\}$ and T.
- Bubble-point temperature calculations: compute $\{y_i\}$ and T at specified $\{x_i\}$ and P.
- Dew-point pressure calculations: compute $\{x_i\}$ and P at specified $\{y_i\}$ and T.
- Dew-point temperature calculations: compute $\{x_i\}$ and T at specified $\{y_i\}$ and P.
- Flash calculations: compute $\{x_i\}$, $\{y_i\}$ and vapor-to-feed mole ratio at specified T and P.

In this work, both bubble-point pressure and bubble-point temperature calculations are carried out by using the $\phi-\phi$ method. Equation (5.0.3) can be simplified and rewritten as

$$x_i\hat{\phi}_i^L(T,P,x) = y_i\hat{\phi}_i^V(T,P,y) \tag{5.0.4}$$

5.1 Application of the Reformulated PR Equations to VLE Calculations

The reformulated PR equations developed in Chapter 3 are applied to VLE calculations of binary associating systems. Because the association is very weak in vapor phase, the thermodynamic relation to calculate VLE can be approximated by the following equation for associating substances when the infinite linear association model is incorporated into the original PR EOS (Model PPR-1/Model PPR-3).

$$f_i = f_{i1} \tag{5.1.1}$$

where f_i is the fugacity of associating species *i* and f_{i1} is the fugacity of the monomer of component *i*, which is expressed as

$$f_{i1} = P\hat{\phi}_{i1}z_{i1} \tag{5.1.2}$$

$\hat{\phi}_{i1}$ and z_{i1} are the fugacity coefficient and true mole fraction of monomer species *i*, respectively.

Following the VLE criterion, one has

$$P\hat{\phi}_{i1}^V z_{i1}^V = P\hat{\phi}_{i1}^L z_{i1}^L \tag{5.1.3}$$

If the monomer-dimer association model is incorporated into the PR EOS (Model PPR-2/Model PPR-4), then the equilibrium criterion is used for both the monomer and dimer of associating species *i*. The corresponding fugacity expressions for the monomer and dimer are, respectively, given by

$$f_{i1}^{V} = f_{i1}^{L} \tag{5.1.4}$$

$$f_{i2}^{V} = f_{i2}^{L} \tag{5.1.5}$$

Equation (5.1.4) can be expanded using Equation (5.1.3), and Equation (5.1.5) is rewritten as

$$P\hat{\phi}_{i2}^{V} z_{i2}^{V} = P\hat{\phi}_{i2}^{L} z_{i2}^{L} \tag{5.1.6}$$

For non-associating species *k*, the fugacity coefficient satisfies the following equilibrium expression:

$$P\hat{\phi}_{k}^{V} z_{k}^{V} = P\hat{\phi}_{k}^{L} z_{k}^{L} \tag{5.1.7}$$

By using the mixing rules suggested by Hu *et al.* (1984) and the thermodynamic relation, Equation (3.1.5), one can obtain the fugacity coefficient expression for the *j*-mer of the associating species *i*:

$$\hat{\phi}_{ij} = \frac{n_T}{n_0}\left[\frac{RT}{P(v-\bar{b})}\right]\left(\frac{v+(1+\sqrt{2})\bar{b}}{v+(1-\sqrt{2})\bar{b}}\right)^{\frac{-\bar{a}[1+jn_T/n_0(\gamma_{i1}-1)]}{2\sqrt{2}\bar{b}RT}} \exp\left[j\frac{n_T}{n_0}\left(\frac{b_{i1}}{\bar{b}}\right)(Z-1)\right] \tag{5.1.8}$$

and that for the fugacity coefficient of the non-associating component *k*

$$\hat{\phi}_{k} = \frac{n_T}{n_0}\left[\frac{RT}{P(v-\bar{b})}\right]\left(\frac{v+(1+\sqrt{2})\bar{b}}{v+(1-\sqrt{2})\bar{b}}\right)^{\frac{-\bar{a}n_T/n_0(\gamma_k-1)}{2\sqrt{2}\bar{b}RT}} \exp\left[\frac{n_T}{n_0}\left(\frac{b_k}{\bar{b}}\right)(Z-1)\right] \tag{5.1.9}$$

Similarly, the fugacity coefficient expressions for the *j*-mer of the associating species *i* and for the non-associating component *k*, using the mixing rules suggested by Heidemann and Prausnitz (1976), have the following forms, respectively:

$$\hat{\phi}_{ij} = \frac{n_T}{n_0}\left[\frac{RT}{P(v-\bar{b})}\right]\left(\frac{v+(1+\sqrt{2})\bar{b}}{v+(1-\sqrt{2})\bar{b}}\right)^{\frac{-j\bar{a}\gamma_{i1}}{2\sqrt{2}\bar{b}RT}} \exp\left[j\frac{n_T}{n_0}\left(\frac{b_{i1}}{\bar{b}}\right)(Z-1)\right] \tag{5.1.10}$$

$$\hat{\phi}_{k} = \frac{n_T}{n_0}\left[\frac{RT}{P(v-\bar{b})}\right]\left(\frac{v+(1+\sqrt{2})\bar{b}}{v+(1-\sqrt{2})\bar{b}}\right)^{\frac{-\bar{a}\gamma_k}{2\sqrt{2}\bar{b}RT}} \exp\left[\frac{n_T}{n_0}\left(\frac{b_k}{\bar{b}}\right)(Z-1)\right] \tag{5.1.11}$$

where the expression of γ_m is given by

$$\gamma_m = \frac{2\sum_p x_p (a_p a_m)^{0.5}(1-\delta_{pm})}{\bar{a}} - \frac{b_m}{\bar{b}} \qquad (5.1.12)$$

5.1.1 Bubble-point Pressure Calculations

The reformulated equations with parameters determined from pure component data have been employed to calculate VLE in binary systems. The bubble-point pressure calculations are carried out according to the following computational procedures:

1. Calculate the physical parameters a_i and b_i for pure components, and the chemical parameter K_i for pure associating components. The parameter expressions in the reformulated equations have been presented in Chapter 4.
2. Guess initial bubble-point pressure. The initial value of the bubble-point pressure is estimated by assuming ideal vapor and liquid mixtures,

   $$P = \sum P_i^{sat} x_i \qquad (5.1.1.1)$$

   where the vapor pressure of pure components is obtained from the following regression equation (Daubert and Danner, 1989):

   $$\ln P_i^{sat} = A + \frac{B}{T} + C \ln T + DT^E \qquad (5.1.1.2)$$

   where A, B, C, D, E in Equation (5.1.1.2) are coefficients given in Appendix A; T is temperature in K and P_i^{sat} is the saturation pressure in Pa.
3. Calculate the vapor phase mole fraction y_i from the following equation:

   $$y_i = P_i^{sat} x_i / P \qquad (5.1.1.3)$$

4. Evaluate the parameters $\bar{a}$ and $\bar{b}$ for both phases of the mixture by means of two different mixing rules and correlated binary interaction parameter, δ_{AB}.
5. Calculate the vapor and liquid phase molar volumes from the reformulated equations.
6. Calculate the fugacity coefficients of component i in both vapor and liquid phases from Equations (5.1.8 - 5.1.12).
7. Calculate the true mole fraction z_i^V for vapor phase using

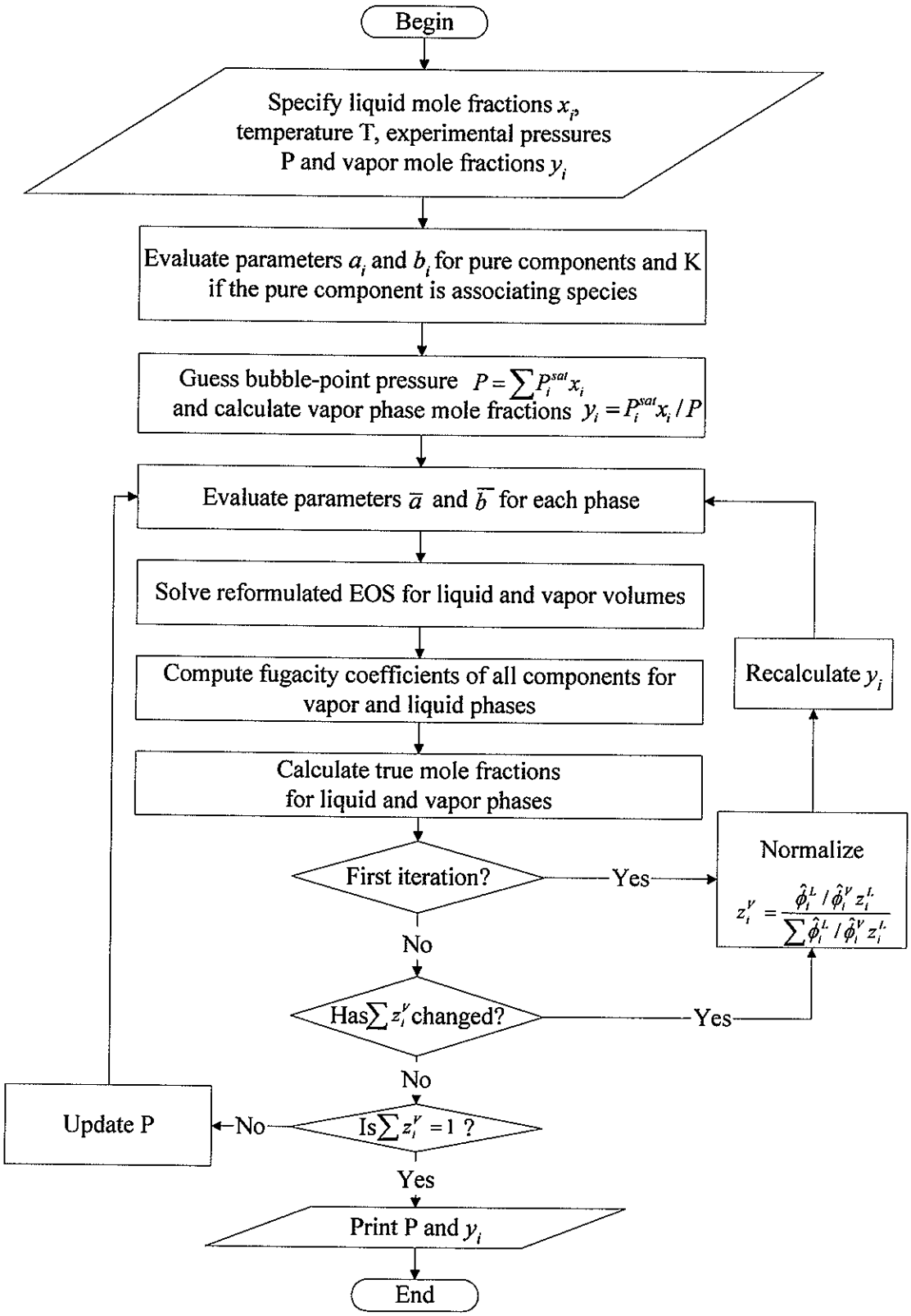

Figure 5.1: Block Diagram for Bubble-point Pressure Calculations

$$z_i^V = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V} z_i^L \qquad (5.1.1.4)$$

where the true mole fraction, z_i^L for the liquid phase is obtained through its relation with the apparent liquid mole fraction, x_i of species *i*.

8. For the first iteration, normalize z_i^V using

$$z_i^V = \frac{\phi_i^L z_i^L / \hat{\phi}_i^V}{\sum \phi_i^L z_i^L / \hat{\phi}_i^V} \qquad (5.1.1.5)$$

and calculate y_i according to the relation between z_i^V and y_i, then go back to step 4. For other iterations, check if the sum of calculated z_i^V has changed compared with the sum calculated from the previous iteration. If so, normalize z_i^V and calculate y_i and return to step 4 again until the change in the sum of z_i^V is less than the tolerance.

9. If the condition is met that the change in the sum of z_i^V is less than the tolerance, then one checks to make sure the true vapor mole fractions sum to 1. If not, we iterate on the pressure guess using Equation (5.1.1.6) until they do.

$$P = P(2 - 1/\sum z_i^V) \qquad (5.1.1.6)$$

When the iterations are done, the final pressure, P, and vapor compositions are the bubble-point pressure and the vapor phase composition y_i.

A schematic block diagram for bubble-point pressure calculations is shown in Figure 5.1.

5.1.2 Bubble-point Temperature Calculations

The bubble-point temperature calculations can be obtained by making some slight changes such as specifying the pressure, P, and adjusting the temperature, T, instead of the pressure P and recalculating the pure component properties in the iteration sequence, although the algorithm described above is specific to the bubble-point pressure calculations. The following empirical formula is used to guess the initial bubble-point temperature:

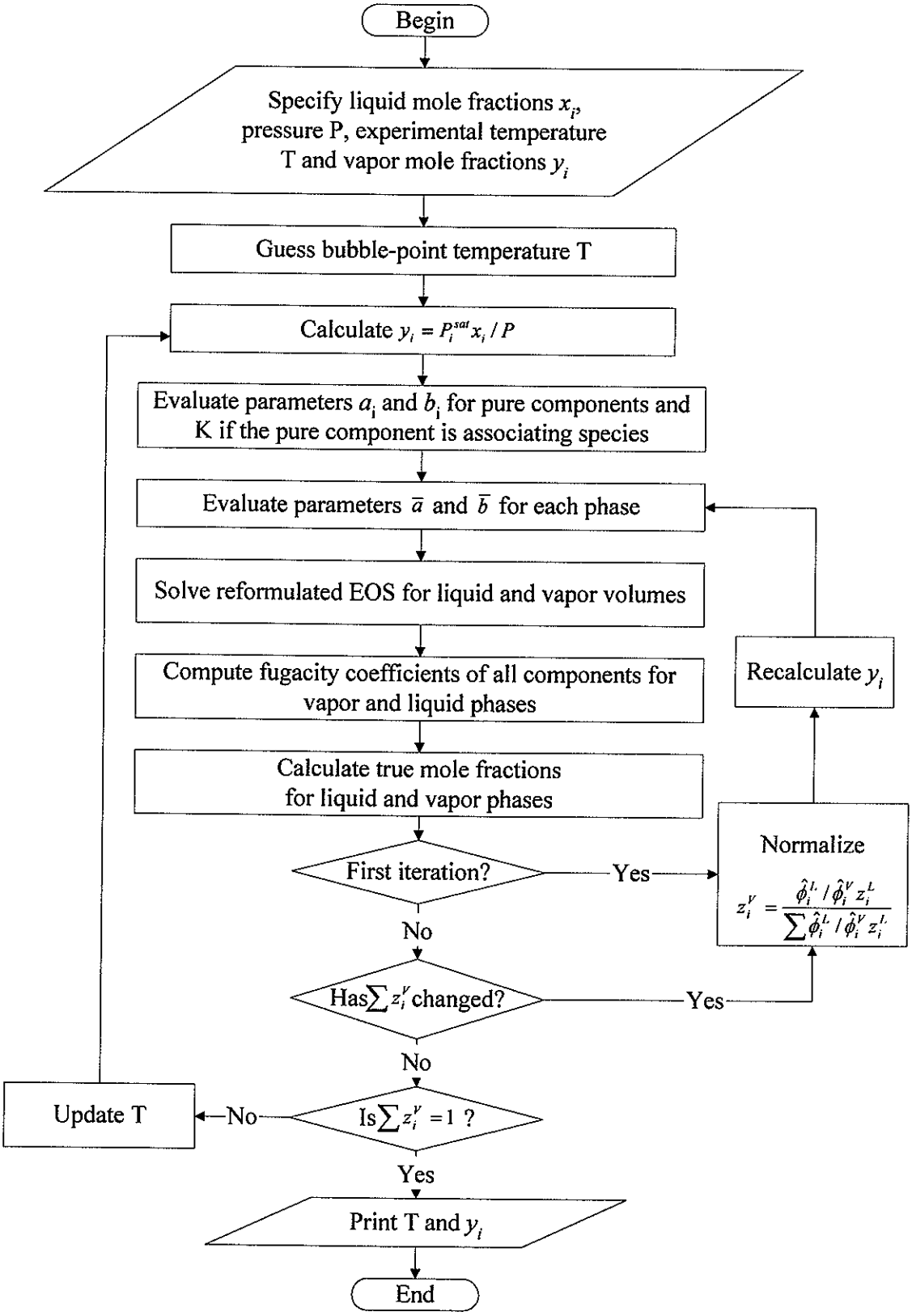

Figure 5.2: Block Diagram for Bubble-point Temperature Calculations

$$T_{initial} = \sum T_i x_i \qquad (5.1.2.1)$$

where x_i refers to the apparent liquid mole fraction of component i; T_i is the initial temperature of component i calculated using Equation (5.1.1.2). The updated temperature value can be obtained via the following expression (Peng, 1991):

$$T = T\left\{1 - T/\left[5.373\sum(1+\omega_i T_{ci} z_i^V)\right]\left\{\sum z_i^V - 1\right\}\right\} \qquad (5.1.2.2)$$

where ω_i and T_{ci} are the acentric factor and critical temperature of species i, respectively. A schematic block diagram for bubble-point temperature calculations is given in Figure 5.2.

5.2 Results and Discussion

The reformulated equations have been used to represent the VLE of associating systems. For a binary system involving the associating species A and non-associating species B, only one binary interaction parameter δ_{AB} is needed to calculate the energy parameter of a mixture. For a binary system in which both components A and B are associating species, an additional binary interaction parameter c_{AB} is needed to calculate the association constant, K_{AB} for the cross associating species, AB, when it is assumed that K_{AB} can be expressed as

$$\ln K_{AB} = \frac{(E_A + E_B)}{2T} + c_{AB} \qquad (5.2.1)$$

where E_A and E_B are the parameters of associating species A and B in Equation (4.6), respectively. The values of parameters for pure components are given in Chapter 4.

The binary interaction parameters are usually calculated by regression analysis of experimental phase equilibrium data. If the experimental *P-x-y* data at a specified temperature are available, the objective function for isothermal VLE is

$$OF = \frac{1}{N}\sum_{i=1}^{N}\frac{|P_{\exp,i} - P_{cal,i}|}{P_{\exp,i}} + \frac{1}{N}\sum_{i=1}^{N}|y_{\exp,i} - y_{cal,i}| \qquad (5.2.2)$$

where P is the pressure in bar, y is the vapor phase mole fraction and N is the number of experimental data points. The subscript *exp* refers to the experimental data and *cal* stands for the calculated results.

If the experimental *T-x-y* data at a specified pressure are provided, then the objective function for isobaric VLE can be expressed as follows:

$$OF = \frac{10}{N}\sum_{i=1}^{N}\frac{|T_{\exp,i} - T_{cal,i}|}{T_{\max}} + \frac{1}{N}\sum_{i=1}^{N}|y_{\exp,i} - y_{cal,i}| \qquad (5.2.3)$$

where T is the temperature in K and *max* refers to the maximum value in the given set of experimental data. The weighting factor of 10 is applied to the first term in Equation (5.2.3).

The objective function for the isobaric VLE, Equation (5.2.3), is defined in order to make the first term and the second term of Equation (5.2.3) of the same order of magnitude to the changes in the binary interaction parameters. The programs for the VLE calculations of the three models used are attached in Appendix B.

The quality of the VLE representations obtained from the different reformulated equations can be assessed by referring to the average absolute deviation (AAD) values presented in Tables 5.1 - 5.5 for selected binary associating systems under isothermal and isobaric conditions. The sources of the experimental data used to determine the binary interaction parameter values are also indicated. The AAD values as reported for the Wilson equation (Wilson, 1964) are also presented in these tables for comparison. The average absolute deviation (AAD) of the calculated results from the experimental data in these tables is defined as

$$\Delta Q = \frac{\sum_{i=1}^{N}|Q_{cal,i} - Q_{\exp,i}|}{N} \qquad (5.2.4)$$

where Q stands for the bubble-point pressure P, the bubble-point temperature T or the vapor phase mole fraction y.

The accuracy of the isothermal and isobaric VLE results of carboxylic acid+hydrocarbon systems obtained by means of Models PPR-2 and PPR-4 is comparable to phase equilibrium values obtained from the Wilson equation, the Hong-Hu equation (Hong and Hu, 1989) and the AMH equation (Nan *et al.*, 2001a). The corresponding values under the isothermal and isobaric conditions are presented in Tables 5.1 and 5.2, respectively. In particular, for the isothermal systems, the overall AAD values of the bubble-point pressure are 0.83, 1.52, and 0.44 kPa, respectively, for

Models PPR-2, PPR-4 and the Wilson equation. The corresponding overall AAD values of the calculated vapor phase compositions in terms of mole fractions are 0.0204, 0.0248, and 0.0364. It can also be seen that the binary interaction parameters are dependent on the temperature although the dependency does not appear to be very large in terms of the overall correction to the energy parameter. For isobaric systems, the overall AAD values of the bubble-point temperature are 0.73, 0.58, 0.85 K for Models PPR-2, PPR-4 and the Wilson equation, respectively. The corresponding overall AAD values of the calculated vapor phase compositions in terms of mole fractions are 0.0184, 0.0175, and 0.0182, respectively.

A comparison is made of the results based on the reformulated models with the calculated results obtained from the use of the existing models (Hong-Hu equation and AMH equation). The experimental data used by Nan *et al.* (2001a) are different from the ones used in this work in terms of the number of data for some systems, and the data sources were not indicated in the work of Hong and Hu (1989). In addition, the reformulated equations have been applied to the VLE calculations of 21 carboxylic acid+hydrocarbon systems whereas Hong and Hu (1989) and Nan *et al.* (2001a) only chose 8 carboxylic acid+hydrocarbon systems to test their models. It is shown that, in general, the quality of the results obtained by means of Models PPR-2 and PPR-4 are seen to be as good as that of the results generated by means of two existing models and are clearly superior to the results from the Wilson equation.

The calculated VLE results obtained from Model PPR-3 for the alkanol+hydrocarbon systems and the comparison with those of the Wilson equation under isothermal conditions, and the comparison with the calculated values from both the Wilson equation and the AMH equation under isobaric conditions are listed in Tables 5.3 and 5.4, respectively. The overall AAD values using Model PPR-3 for the VLE calculations of the alkanol+hydrocarbon systems are higher than the corresponding values reported from the Wilson equation and the AMH equation because of a much broader range of systems tested in this work.

The isobaric VLE calculated results obtained from Models PPR-2 and PPR-4 and the comparison with those of the Wilson equation for binary systems in which both components are associating species such as acid+alkanol/acid, alkanol+alkanol,

acid/alkanol+polar substance are presented in Table 5.5. The results calculated by means of the reformulated equations using two optimized binary interaction parameters δ_{AB} and c_{AB} are compared with the calculated results based on the Wilson equation and the Hong-Hu equation. It is observed that for a total of 74 systems, the overall AAD values obtained by means of Models PPR-2, PPR-4 are 0.60 K, 0.95 K, respectively, in the bubble-point temperature, and 0.0195, 0.0226 mole fraction, respectively, in the vapor phase composition. The corresponding values obtained from the Wilson equation are 0.83 K in the bubble-point temperature and 0.0170 mole fraction in the vapor phase composition. The overall AAD values of 41 tested systems calculated from the Hong-Hu equation are 0.66 K in the bubble-point temperature and 0.0061 mole fraction in the vapor phase composition. In general, Model PPR-2 based on the monomer-dimer association model and the mixing rules proposed by Hu *et al.* (1984) can be used to obtain good results in view of overall AAD values and the number of tested systems. It should be mentioned that the VLE representations for the systems under isobaric conditions are based on using a constant binary interaction parameter value for each set of data. It is reasonable to anticipate that the errors of the calculations based on the proposed models could be reduced if the binary interaction parameters were allowed to vary with temperature.

Some examples are illustrated in Figures 5.3 - 5.10 comparing the reformulated equations with the original PR EOS in calculating VLE behavior of associating systems.

Figures 5.3 and 5.4 show a comparison for an azeotrope-forming mixture of acetic acid+toluene at 1 atmosphere between Model PPR-2 and the original PR EOS, and Model PPR-4 and the original PR EOS, respectively. All curves represent the best fit of the experimental data with only one non-zero value of binary interaction parameter δ_{AB}. In general, the results obtained from Models PPR-2 and PPR-4 give a better description of the acetic acid+toluene mixture than that of the original PR EOS whereas the azeotropic temperatures calculated from Models PPR-2 and PPR-4 are 103.8°C and 103.5°C, respectively, which are slightly lower than the experimental value of 104.4°C.

The comparison of acetic acid+methanol mixture at 1 atmosphere between Models PPR-2, PPR-4 and the PR EOS are presented in Figures 5.5 and 5.6, respectively. It is interesting to observe that the use of two binary interaction parameters

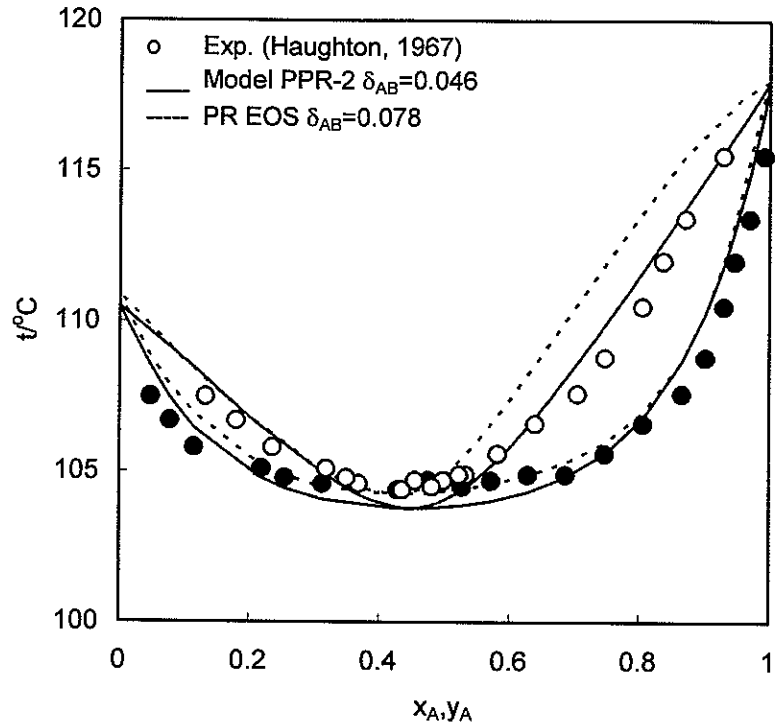

Figure 5.3: VLE for Acetic acid(A)+Toluene(B) System at 1atm from Model PPR-2

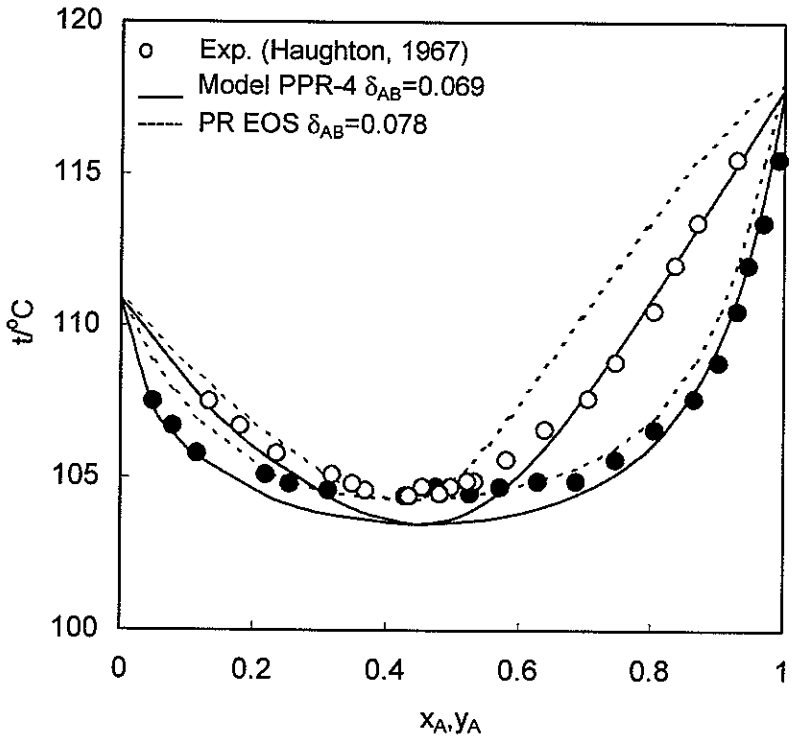

Figure 5.4: VLE for Acetic acid(A)+Toluene(B) System at 1atm from Model PPR-4

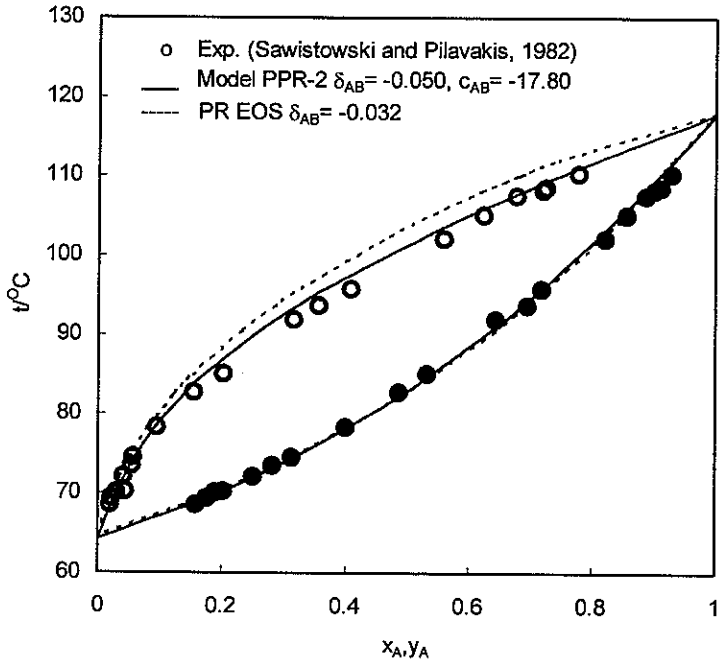

Figure 5.5: VLE for Acetic acid(A)+Methanol(B) System at 1atm from Model PPR-2

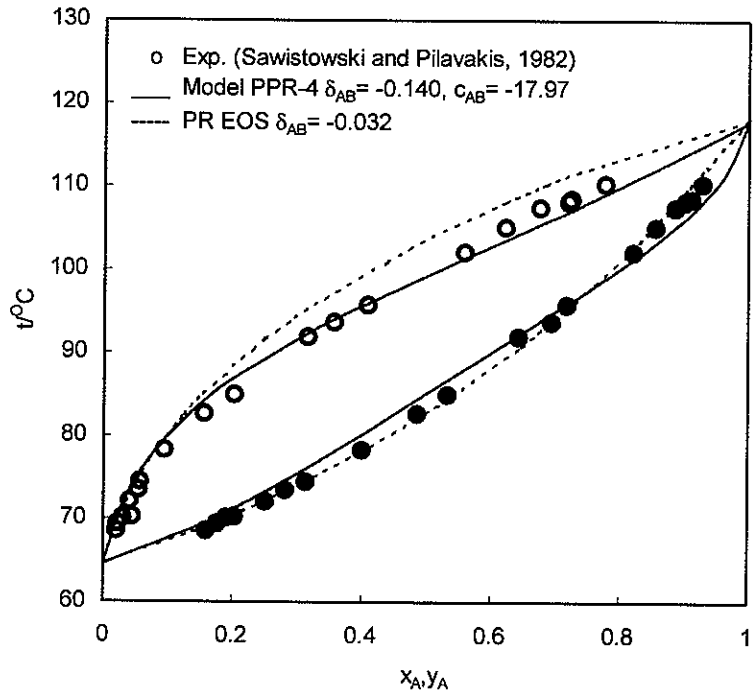

Figure 5.6: VLE for Acetic acid(A)+Methanol(B) System at 1atm from Model PPR-4

can effectively give a good fit to the experimental data. It also can be seen clearly that the reformulated equations are capable of predicting the VLE with reasonable accuracy. The PR EOS, on the other hand, does not do a very good job of presenting the VLE behavior. This is expected as the PR EOS has been designed for hydrocarbons and thus cannot handle polar components such as alkanols, properly. The similar calculations are done on the acetic acid+propionic acid mixture and presented in Figures 5.7 and 5.8.

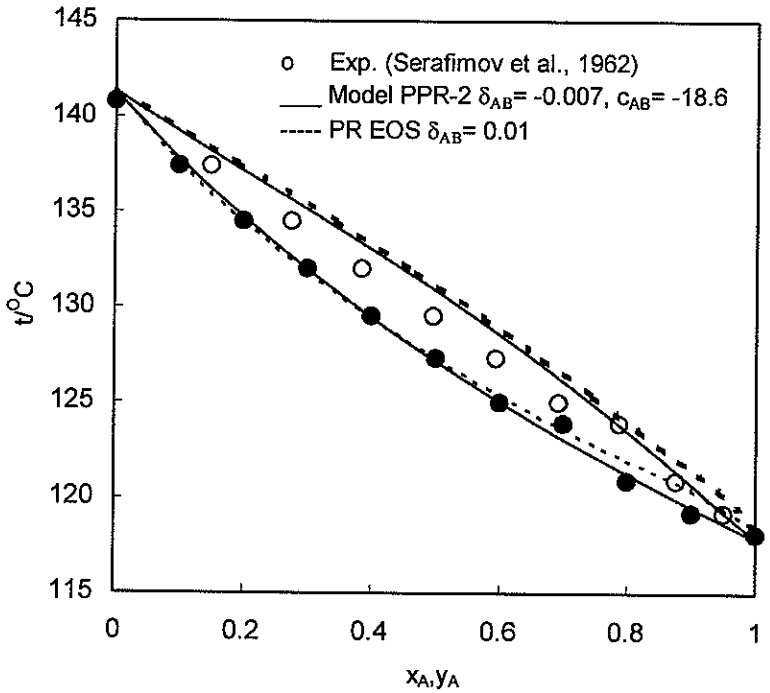

Figure 5.7: VLE for Acetic acid(A)+Propionic acid(B) System at 1atm from Model PPR-2

The Model PPR-3 shows a great improvement over the original PR EOS as observed in Figure 5.9 for the isobaric system ethanol+*p*-xylene at 1 atmosphere. This improvement is largest in the region of low ethanol mole fraction. It should be noted that both approaches use only one binary interaction parameter.

The VLE data of the 1-butanol+benzene mixture at 25°C are illustrated in Figure 5.10. Again Model PPR-3 gives an improvement over the original PR EOS in the bubble-point pressure calculations.

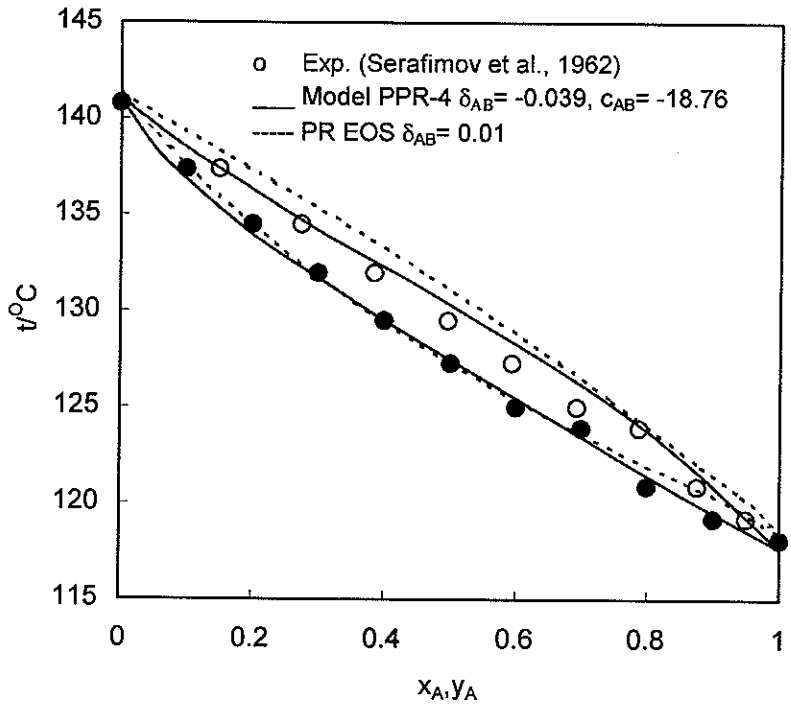

Figure 5.8: VLE for Acetic acid(A)+Propionic acid(B) System at 1atm from Model PPR-4

Figure 5.11 illustrates a comparison of the VLE calculated results obtained from Model PPR-1 with those from Model PPR-3 for a typical system (ethanol+*n*-hexane) at 35°C. It is evident that the performance of Model PPR-3 is better than that of Model PPR-1 when both equations use one binary interaction parameter. Since a reliable prediction of vapor pressure of a pure compound by an equation of state is a prerequisite of its reliability in estimating VLE of binary or multicomponent systems, the relatively larger average AAPD value calculated from Model PPR-1 for vapor pressures of pure associating compounds indicates it is an inferior model to use in predicting satisfactory VLE results for associating systems. Therefore, Model PPR-1 is not used further for analysis of associating systems. The VLE calculations by means of different reformulated equations, with the exception of Model PPR-1, are presented in tables of this Chapter.

Comparisons of the calculated results using the reformulated equations and the experimental data for some selected systems are presented in Appendix D for reference.

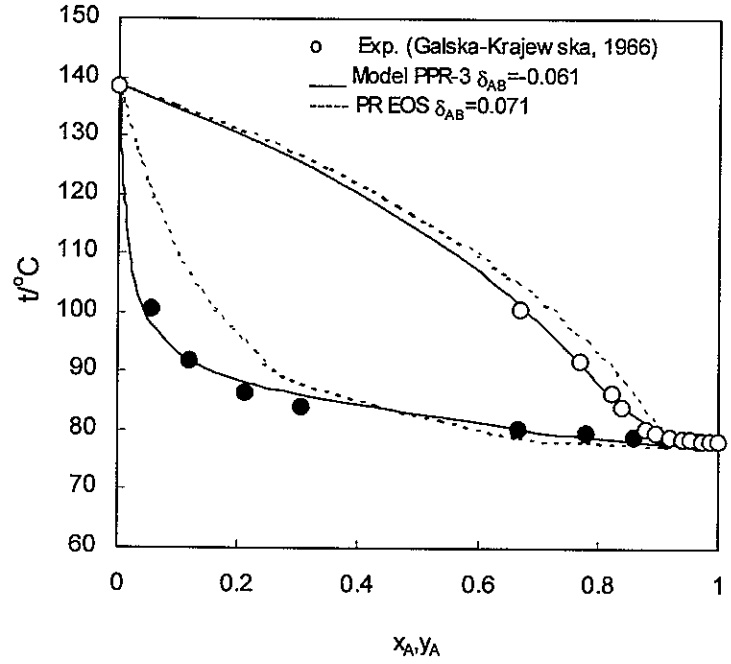

Figure 5.9: VLE for Ethanol(A)+*p*-Xylene(B) System at 1atm from Model PPR-3

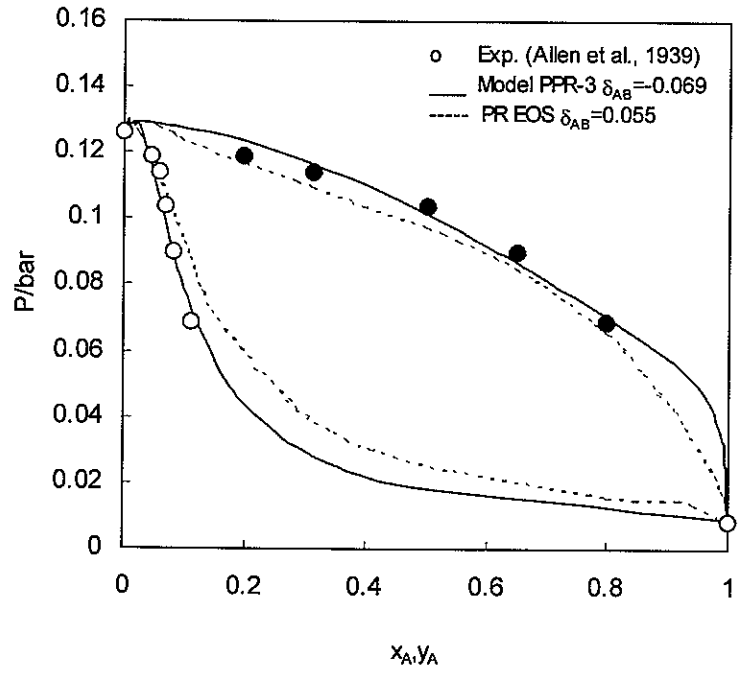

Figure 5.10: VLE for 1-Butanol(A)+Benzene(B) System at 25°C from Model PPR-3

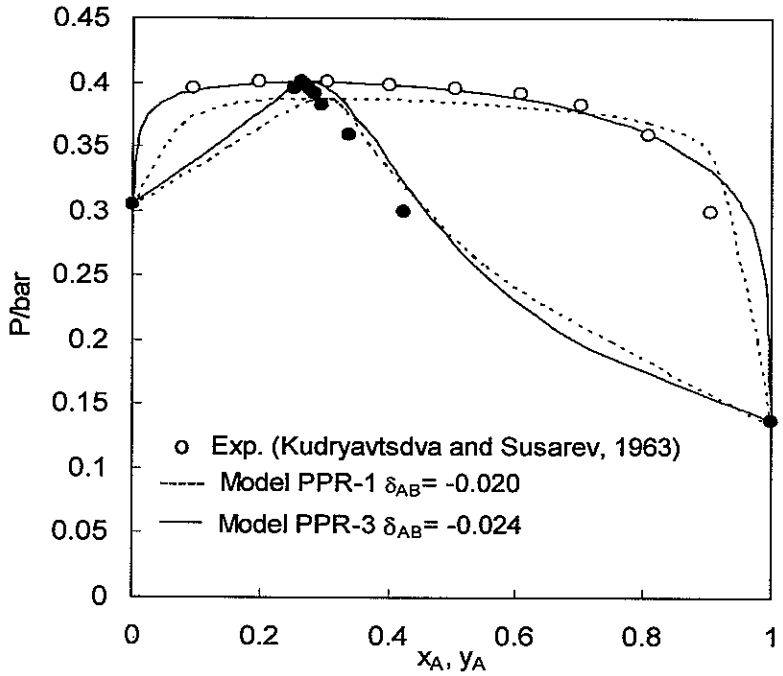

Figure 5.11: VLE for Ethanol(A)+*n*-Hexane(B) System at 35°C from Models PPR-1 and PPR-3

It can be seen from Tables 5.1 and 5.3, although the temperature dependence of the binary interaction parameter δ_{AB} is weak, it has to be taken into account in order to obtain accurate VLE estimates at different temperatures. The temperature dependence of the binary interaction parameter δ_{AB} can be approximated by the following expression:

$$\delta_{AB} = \delta_1 T^2 + \delta_2 T + \delta_3 \qquad (5.2.5)$$

where δ_1, δ_2 and δ_3 are fitting coefficients. For the systems with one set of isothermal VLE data, the coefficients of binary interaction parameters cannot be obtained because only one value of the binary interaction parameter is available. For the systems with two sets of experimental VLE data, the binary parameter δ_{AB} is a linear function of temperature so that the coefficient δ_1 is equal to 0. For the systems with more than two sets of experimental VLE data, the values of coefficients in Equation (5.2.5) are given in Table 5.6 for Model PPR-3 and in Table 5.7 for Models PPR-2 and PPR-4, respectively.

Table 5.1: Results of VLE Calculations for Acid+Hydrocarbon Systems under Isothermal Conditions

VLE System	t/°C	PPR-2			PPR-4			Wilson		N	Data Source
		δ_{AB}	ΔP/kPa	Δy	δ_{AB}	ΔP/kPa	Δy	ΔP/kPa	Δy		
Acetic+Benzene	25	0.058	0.38	0.0165	0.075	0.63	0.0268	0.34	0.0332	18	Lark et al. (1984)
	45	0.065	0.68	0.0135	0.085	1.12	0.0276	0.70	0.0331	18	Lark et al. (1984)
Acetic+Cyclohexane	25	0.091	0.97	0.0331	0.104	2.04	0.0234	n.a.	n.a.	19	Lark et al. (1984)
	45	0.098	1.35	0.0266	0.115	3.95	0.0132	0.91	0.0603	18	Lark et al. (1984)
Acetic+*n*-Heptane	25	0.009	0.40	0.0422	0.085	0.83	0.0322	n.a.	n.a.	15	Lark et al. (1984)
	45	0.029	0.67	0.0224	0.096	1.74	0.0182	0.27	0.0756	15	Lark et al. (1984)
Propionic+Cyclohexane	25	0.096	0.61	0.0224	0.096	0.86	0.0295	0.28	0.0213	18	Lark et al. (1985)
	45	0.101	0.99	0.0195	0.105	1.90	0.0322	0.64	0.0212	18	Lark et al. (1985)
Propionic+*n*-Heptane	25	0.048	0.24	0.0135	0.089	0.36	0.0276	0.16	0.0224	16	Lark et al. (1985)
	45	0.051	0.40	0.0088	0.095	0.83	0.0285	0.24	0.0238	16	Lark et al. (1985)
Valeric+*n*-Heptane	100	0.061	2.44	0.0061	0.083	2.49	0.0135	n.a.	n.a.	13	Lodl and Scheller (1967)
Overall AAD			0.83	0.0204	0.09	1.52	0.0248	0.44	0.0364	184	

Table 5.2: Results of VLE Calculations for Acid+Hydrocarbon Systems under Isobaric Conditions

VLE System	P	PPR-2			PPR-4			Wilson		N	Hong and Hu		Nan et al.		Data Source
	mmHg	δ_{AB}	ΔT/K	Δy	δ_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	ΔT/K	Δy	
Acetic+Benzene	760	0.068	0.41	0.0129	0.050	0.42	0.0129	0.68	0.0097	16	0.80	0.0057	0.71	0.0158	Haughton (1967)
Acetic+Cyclohexane	760	0.078	1.30	0.0222	0.096	0.73	0.0311	1.38	0.0168	12	n.a.	n.a.	n.a.	n.a.	Baradarajan and Satyanarayana (1967)
Acetic+Toluene	760	0.046	0.77	0.0116	0.069	0.32	0.0111	1.08	0.0245	22	n.a.	n.a.	n.a.	n.a.	Haughton (1967)
Acetic+Ethylbenzene	725	0.033	0.84	0.0348	0.066	0.54	0.0339	1.58	0.0286	13	n.a.	n.a.	n.a.	n.a.	Bagga and Raju (1970)
Acetic+*o*-Xylene	27	-0.005	0.33	0.0365	0.066	0.26	0.0365	0.84	0.0626	11	n.a.	n.a.	n.a.	n.a.	Volpicelli and Zizza (1963)
Acetic+*p*-Xylene	725	0.015	0.39	0.0125	0.059	0.51	0.0209	0.88	0.0133	12	n.a.	n.a.	n.a.	n.a.	Bagga and Raju (1970)
Acetic+*n*-Octane	760	0.019	0.80	0.0093	0.101	1.17	0.0149	0.67	0.0224	20	0.60	0.0133	0.39	0.0114	Schicktanz (1937)
Acetic+*n*-Decane	760	-0.007	0.26	0.0091	0.101	0.18	0.0036	0.17	0.0018	11	0.71	0.0088	0.26	0.0026	Zieborak and Brzostowski (1957)
Propionic+Benzene	760	0.076	0.39	0.0082	0.003	0.41	0.0032	0.18	0.0093	14	0.40	0.0076	0.22	0.0030	Malijevska and Pick (1970)
Propionic+Cyclohexane	760	0.113	1.08	0.0153	0.073	0.79	0.0059	0.70	0.0090	14	n.a.	n.a.	n.a.	n.a.	Svitilova et al. (1980)
Propionic+Ethylbenzene	760	0.020	0.99	0.0141	0.026	0.22	0.0129	1.10	0.0145	18	n.a.	n.a.	n.a.	n.a.	Jain et al. (1977a)
Propionic+*m*-Xylene	760	0.017	0.51	0.0094	0.021	0.35	0.0133	0.58	0.0109	15	0.87	0.0053	0.50	0.0133	Jain et al. (1976)

VLE System	P	PPR-2			PPR-4			Wilson		N	Hong and Hu		Nan et al.		Data Source
	mmHg	δ_{AB}	ΔT/K	Δy	δ_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	ΔT/K	Δy	
Propionic+*o*-Xylene	760	0.020	0.20	0.0083	0.017	0.52	0.0115	0.32	0.0024	19	0.23	0.0070	0.76	0.0101	Jain et al. (1977b)
Propionic+*p*-Xylene	760	0.018	0.76	0.0182	0.020	0.37	0.0187	1.25	0.0198	17	1.20	0.0108	0.42	0.0200	Jain et al. (1977a)
Propionic+*n*-Octane	750	0.021	0.70	0.0125	0.054	0.99	0.0152	0.91	0.0241	12	0.72	0.0161	0.57	0.0141	Johnson et al. (1954)
Butyric+*m*-Xylene	760	0.052	1.73	0.0359	0.018	1.71	0.0466	1.84	0.0337	23	n.a.	n.a.	n.a.	n.a.	Jain and Raju (1978)
Butyric+*o*-Xylene	760	0.047	0.79	0.0258	-0.015	0.95	0.0118	1.13	0.0119	18	n.a.	n.a.	n.a.	n.a.	Jain and Raju (1978)
Butyric+*p*-Xylene	760	0.039	1.06	0.0174	-0.005	0.51	0.0253	0.71	0.0309	14	n.a.	n.a.	n.a.	n.a.	Radwan and Hanna (1976)
Butyric+*n*-Octane	760	0.057	0.58	0.0219	0.050	0.28	0.0175	1.00	0.0084	19	n.a.	n.a.	n.a.	n.a.	Radwan and Hanna (1976)
Isobutyric+*p*-Xylene	760	0.052	0.32	0.0189	0.006	0.50	0.0051	0.33	0.0085	21	n.a.	n.a.	n.a.	n.a.	Radwan and Hanna (1976)
Isobutyric+*n*-Octane	760	0.035	1.21	0.0312	0.027	0.50	0.0162	0.51	0.0186	20	n.a.	n.a.	n.a.	n.a.	Radwan and Hanna (1976)
Overall AAD			0.73	0.0184		0.58	0.0175	0.85	0.0182	341	0.69	0.0093	0.48	0.0113	

Table 5.3: Results of VLE Calculations for Alkanol+Hydrocarbon Systems under Isothermal Conditions

VLE System	t/°C	PPR-3			Wilson		N	Data Source
		δ_{AB}	ΔP/kPa	Δy	ΔP/kPa	Δy		
MeOH+Benzene	30	-0.080	0.86	n.a.	0.61	n.a.	10	Schmidt (1926)
	40	-0.065	1.64	0.0328	1.00	0.0111	13	Lee (1931)
	55	-0.076	2.43	0.0178	0.41	0.0072	6	Morachevskii and Komarova (1957)
	80	-0.099	6.71	n.a.	4.00	n.a.	11	Schmidt (1926)
	100	-0.131	15.38	n.a.	9.98	n.a.	11	Schmidt (1926)
MeOH+*n*-Hexane	35	-0.002	1.01	n.a.	0.59	n.a.	24	Wolff and Hoeppel (1968)
	45	0.001	0.76	0.0242	0.61	0.0087	13	Ferguson (1932)
	50	0.000	2.19	n.a.	0.87	n.a.	24	Wolff and Hoeppel (1968)
	60	-0.001	3.64	n.a.	1.24	n.a.	24	Wolff and Hoeppel (1968)
	75	0.003	6.78	n.a.	2.57	n.a.	24	Wolff and Hoeppel (1968)
MeOH+Cyclohexane	35	-0.013	1.27	0.0269	0.70	0.0100	6	Marinichev and Susarev (1965)
	45	-0.013	3.62	0.0490	1.98	0.0204	13	Madhavan and Murti (1966)
MeOH+Cyclohexane	55	-0.013	5.30	0.0395	2.49	0.0151	11	Madhavan and Murti (1966)
EtOH+*n*-Butane	25	-0.046	15.10	n.a.	n.a.	n.a.	24	Holderbaum et al. (1991)
	51	-0.043	19.91	n.a.	n.a.	n.a.	24	Holderbaum et al. (1991)
	73	-0.042	28.02	n.a.	n.a.	n.a.	24	Holderbaum et al. (1991)
EtOH+Benzene	25	-0.077	0.19	n.a.	n.a.	n.a.	11	Smith and Robinson (1970)
	45	-0.082	0.88	0.0318	0.10	0.0033	12	Brown and Smith (1954)
	50	-0.082	1.10	0.0248	0.46	0.0042	16	Zharov and Morachevskii (1963)
	60	-0.082	2.25	0.0383	0.93	0.0059	12	Udovenko and Fatkulina (1952)
EtOH+Cyclohexane	25	-0.029	0.28	0.0259	0.15	0.0093	9	Washburn and Handorf (1935)
	35	-0.028	0.43	0.0166	0.18	0.0010	9	Scatchard and Satkifwicz (1964)
	50	-0.029	0.70	0.0196	0.18	0.0010	8	Scatchard and Satkifwicz (1964)
	65	-0.029	1.29	0.0181	0.31	0.0010	9	Scatchard and Satkifwicz (1964)
EtOH+*n*-Hexane	25	-0.028	0.36	0.0130	0.16	0.0021	9	Smith and Robinson (1970)
	35	-0.024	0.44	0.0198	0.25	0.0039	11	Kudryavtsdva and Susarev (1963)

VLE System	t/°C	PPR-3			Wilson		N	Data Source
		δ_{AB}	ΔP/kPa	Δy	ΔP/kPa	Δy		
EtOH+*n*-Hexane	45	-0.020	0.82	0.0249	0.30	0.0072	11	Kudryavtsdva and Susarev (1963)
	55	-0.022	0.98	0.0247	0.67	0.0066	11	Kudryavtsdva and Susarev (1963)
	60	-0.022	0.95	0.0323	1.36	0.0075	8	Lindberg and Tassios (1971)
EtOH+Toluene	35	-0.070	0.47	0.0235	n.a.	n.a.	12	Kretschmer and Wiebe, 1949
	50	-0.070	0.83	0.0227	0.39	0.0054	9	Lehfeldt (1898)
	55	-0.070	1.14	0.0172	n.a.	n.a.	12	Kretschmer and Wiebe, 1949
	60	-0.065	1.92	0.0269	1.66	0.0138	11	Wright (1933)
	70	-0.062	3.07	0.0244	2.04	0.0119	11	Wright (1933)
	80	-0.061	4.78	0.0232	2.43	0.0126	11	Wright (1933)
EtOH+*n*-Heptane	30	-0.021	0.37	0.0238	0.26	0.0116	10	Ferguson et al. (1933)
	40	-0.029	0.68	0.0226	0.34	0.0106	10	Ratcliff and Chao (1969)
	50	-0.031	0.85	0.0376	1.88	0.0166	12	Smith and Engel (1929)
	70	-0.005	1.25	0.0065	1.65	0.0085	11	Ramalho and Delnas (1968)
	80	0.014	3.14	0.0037	4.15	0.0114	11	Ramalho and Delnas (1968)
	90	0.028	3.89	0.0098	5.53	0.0119	11	Ramalho and Delnas (1968)
1-PrOH+Benzene	30	-0.064	0.38	n.a.	0.13	n.a.	11	Schmidt (1926)
	45	-0.080	0.78	0.0200	0.10	0.0127	11	Brown and Smith (1954)
	60	-0.095	1.53	0.0333	0.33	0.0065	15	Udovenko and Mazanko (1972)
	75	-0.102	2.41	0.0272	0.69	0.0150	13	Fu and Lu (1966)
1-PrOH+Cyclohexane	55	-0.057	2.17	0.0420	0.44	0.0166	17	Strubl et al. (1970)
	65	-0.068	4.22	0.0505	0.89	0.0097	14	Strubl et al. (1970)
1-PrOH+*n*-Hexane	45	-0.032	0.37	0.0121	0.76	0.0047	5	Brown et al. (1969)
1-PrOH+*n*-Heptane	75	-0.045	1.82	0.0154	2.08	0.0277	14	Fu and Lu (1966)
1-PrOH+*n*-Nonane	25	-0.017	0.02	0.0118	n.a.	n.a.	17	Heintz et al. (1986a)
1-PrOH+*n*-Decane	90	-0.029	1.41	0.0048	0.52	0.0017	11	Ratcliff and Chao (1969)
	95	-0.052	3.73	0.0223	1.18	0.0067	12	Ellis et al. (1960)
2-PrOH+Benzene	30	-0.092	0.82	0.0530	0.98	0.0402	14	Udovenko and Mazanko (1967)
	45	-0.096	0.92	0.0293	0.17	0.0076	12	Brown and Smith (1956)
	50	-0.097	0.68	0.0103	1.01	0.0110	6	Zharov et al (1965)
	60	-0.100	1.38	0.0293	2.38	0.0238	14	Udovenko and Mazanko (1967)
	70	-0.109	2.19	0.0182	0.63	0.0057	10	Nagata et al. (1973)

VLE System	t/°C	PPR-3			Wilson		N	Data Source
		δ_{AB}	ΔP/kPa	Δy	ΔP/kPa	Δy		
2-PrOH+Cyclohexane	40	-0.051	0.36	0.0089	0.59	0.0095	6	Storonkin and Morachevskii (1956)
	55	-0.056	0.35	0.0132	0.72	0.0072	5	Storonkin and Morachevskii (1956)
	60	-0.054	1.08	0.0174	0.70	0.0090	10	Nagata et al. (1973)
	69	-0.056	0.77	0.0148	1.00	0.0052	6	Storonkin and Morachevskii (1956)
2-PrOH+*n*-Hexane	60	-0.042	0.98	0.0221	0.67	0.0155	18	Heintz et al. (1986)
2-PrOH+*n*-Heptane	25	-0.034	0.07	0.0177	n.a.	n.a.	18	Heintz et al. (1986)
	45	-0.040	0.49	0.0219	0.37	0.0129	17	Heintz et al. (1986)
	60	-0.042	0.99	0.0221	0.67	0.0115	18	Heintz et al. (1986)
2-PrOH+*n*-Decane	90	-0.027	2.35	0.0027	1.47	0.0006	7	Ratcliff and Chao (1969)
1-BuOH+Benzene	25	-0.069	0.24	0.0055	0.61	0.0059	7	Allen et al. (1939)
	45	-0.069	0.58	0.0070	0.24	0.0034	9	Brown and Smith (1959)
1-BuOH+Cyclohexane	80	-0.059	3.51	0.0135	2.32	0.0264	11	Ramalho and Delnas (1968)
	90	-0.054	3.02	0.0162	2.96	0.0195	11	Ramalho and Delnas (1968)
	100	-0.053	2.80	0.0155	3.51	0.0210	11	Ramalho and Delnas (1968)
	110	-0.053	4.98	0.0204	3.32	0.0236	11	Ramalho and Delnas (1968)
1-BuOH+*n*-Hexane	25	-0.045	0.62	0.0065	2.23	0.0059	9	Smirnova et al. (1969)
	50	-0.035	1.56	0.0125	n.a.	n.a.	14	Heintz et al. (1986)
1-BuOH+Toluene	90	-0.078	1.16	0.0247	1.68	0.0086	17	Seetharamaswamy et al. (1969)
	100	-0.082	0.87	0.0126	0.75	0.0087	10	Gorbunov et al. (1968)
1-BuOH+*n*-Heptane	50	-0.034	0.24	0.0149	0.17	0.0119	14	Smith and Engel (1929)
1-BuOH+*n*-Octane	100	-0.034	0.55	n.a.	n.a.	n.a.	14	Gierycz et al. (1988)
	110	-0.035	0.75	n.a.	n.a.	n.a.	14	Gierycz et al. (1988)
1-BuOH+*n*-Nonane	50	-0.025	0.04	0.0074	n.a.	n.a.	15	Heintz et al. (1986)
1-BuOH+*n*-Decane	100	-0.021	1.45	0.0094	1.64	0.0127	21	Lee and Scheller (1967)
	110	-0.029	1.11	n.a.	n.a.	n.a.	14	Gierycz et al. (1988)
2-BuOH+Benzene	45	-0.093	0.60	0.0127	0.10	0.0024	12	Brown et al. (1969)
	60	-0.093	1.28	0.0233	1.56	0.0099	9	Echevarria (1973)
	70	-0.110	1.38	0.0156	0.33	0.0119	10	Echevarria (1973)
	80	-0.116	1.99	0.0141	1.71	0.0073	10	Echevarria (1973)
2-BuOH+*n*-Hexane	60	-0.053	1.50	0.0145	0.64	0.0038	11	Hanson and Van Winkle (1967)
Tert-BuOH+Benzene	45	-0.130	0.64	0.0225	0.13	0.0075	13	Brown et al. (1969)
	60	-0.131	0.67	0.0132	1.19	0.0097	10	Echevarria (1973)
	70	-0.139	0.66	0.0140	1.46	0.0076	10	Echevarria (1973)

VLE System	t/°C	PPR-3			Wilson		N	Data Source
		δ_{AB}	ΔP/kPa	Δy	ΔP/kPa	Δy		
Tert-BuOH+Benzene	80	-0.150	19.43	0.0175	11.98	0.0228	8	Echevarria (1973)
Iso-BuOH+Benzene	45	-0.076	0.64	0.0102	0.12	0.0017	12	Brown et al. (1969)
	60	-0.088	0.97	0.0156	0.50	0.0174	10	Echevarria (1973)
	70	-0.087	1.84	0.0117	0.80	0.0168	10	Echevarria (1973)
	80	-0.092	1.81	0.0195	2.05	0.0117	10	Echevarria (1973)
Iso-BuOH+Toluene	80	-0.078	0.49	0.0141	0.78	0.0095	9	Susarev and Toikka (1973)
	100	-0.085	0.83	0.0110	1.08	0.0090	9	Susarev and Toikka (1973)
Iso-BuOH+*n*-Heptane	25	-0.028	0.13	0.0164	n.a.	n.a.	16	Heintz et al. (1986)
PeOH+*n*-Hexane	25	-0.047	0.68	0.0019	0.23	0.0005	11	Sayegh and Ratcliff (1976)
PeOH+Toluene	70	-0.077	0.60	0.0223	0.19	0.0101	20	Sadler et al. (1971)
	90	-0.082	0.87	0.0167	0.40	0.0054	20	Sadler et al. (1971)
	110	-0.087	1.06	0.0115	1.13	0.0093	23	Sadler et al. (1971)
PeOH+*n*-Heptane	75	-0.058	1.76	0.0279	n.a.	n.a.	21	Machova et al. (1988)
PeOH+*n*-Heptane	85	-0.051	2.18	n.a.	n.a.	n.a.	20	Machova et al. (1988)
	95	-0.049	2.71	n.a.	n.a.	n.a.	20	Machova et al. (1988)
HeOH+Cyclohexane	50	-0.039	0.98	0.0028	0.99	0.0021	13	Svoboda et al. (1971)
	60	-0.047	2.16	0.0025	1.44	0.0029	14	Svoboda et al. (1971)
	81	-0.050	3.49	0.0067	2.26	0.0026	18	Svoboda et al. (1971)
HeOH+*n*-Hexane	25	-0.052	0.81	n.a.	n.a.	n.a.	9	Wieczorek and Stecki (1978a)
	35	-0.052	1.27	n.a.	n.a.	n.a.	9	Wieczorek and Stecki (1978a)
	45	-0.053	2.00	n.a.	n.a.	n.a.	9	Wieczorek and Stecki (1978a)
	55	-0.054	2.91	n.a.	n.a.	n.a.	9	Wieczorek and Stecki (1978a)
HeOH+*n*-Hexane	65	-0.055	3.94	n.a.	n.a.	n.a.	9	Wieczorek and Stecki (1978a)
OcOH+*n*-Hexane	40	-0.070	2.58	0.0004	n.a.	n.a.	10	Heintz et al. (1986)
DeOH+*n*-Hexane	10	-0.057	0.66	n.a.	n.a.	n.a.	10	Wieczorek (1979)
	30	-0.057	1.56	n.a.	n.a.	n.a.	10	Wieczorek (1979)
	50	-0.059	3.41	n.a.	n.a.	n.a.	10	Wieczorek (1979)
DodeOH+*n*-Hexane	25	-0.043	0.91	n.a.	n.a.	n.a.	10	Heintz et al. (1986)
	35	-0.067	2.04	n.a.	n.a.	n.a.	9	Wieczorek (1978b)
	45	-0.068	3.09	n.a.	n.a.	n.a.	9	Wieczorek (1978b)
	55	-0.069	4.35	n.a.	n.a.	n.a.	9	Wieczorek (1978b)
	65	-0.070	5.84	n.a.	n.a.	n.a.	9	Wieczorek (1978b)
	70	-0.071	6.15	n.a.	n.a.	n.a.	9	Wieczorek (1978b)
Overall AAD			2.41	0.0190	1.33	0.0100	1521	

Table 5.4: Results of VLE Calculations for Alkanol+Hydrocarbon Systems under Isobaric Conditions

VLE System	P	PPR-3			Wilson		N	Nan et al.		Data Source
	mmHg	δ_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
MeOH+Benzene	760	-0.091	0.66	0.0302	0.25	0.0041	19	0.66	0.0159	Cabezas et al. (1985)
MeOH+Cyclohexane	760	-0.004	0.63	0.0204	0.92	0.0095	13	0.21	0.0095	Budantseva et al. (1975a)
MeOH+*n*-Hexane	760	0.003	0.56	0.0114	0.55	0.0159	13	1.32	0.0283	Budantseva et al. (1975a)
MeOH+Toluene	760	-0.057	0.67	0.0100	0.10	0.0080	10	1.09	0.0167	Benedict et al. (1945)
MeOH+*n*-Heptane	760	0.003	0.50	0.0137	0.52	0.0064	13	0.38	0.0133	Budantseva et al. (1975a)
MeOH+*m*-Xylene	760	-0.046	1.81	0.0130	0.63	0.0108	13	n.a.	n.a.	Budantseva et al. (1975b)
MeOH+*p*-Xylene	760	-0.045	1.59	0.0121	0.60	0.0099	13	n.a.	n.a.	Budantseva et al. (1975b)
MeOH+*n*-Octane	760	0.012	0.50	0.0040	0.31	0.0033	13	n.a.	n.a.	Budantseva et al. (1975a)
MeOH+*n*-Decane	760	0.023	0.97	0.0032	0.39	0.0003	9	n.a.	n.a.	Ogorodnikov et al. (1960)
EtOH+Benzene	760	-0.094	0.52	0.0412	0.45	0.0105	17	n.a.	n.a.	Cabezas et al. (1985)
EtOH+*p*-Xylene	760	-0.060	0.81	0.0111	0.28	0.0064	13	n.a.	n.a.	Galska-Krajewska (1966)
EtOH+*n*-Octane	760	-0.028	0.51	0.0279	1.09	0.0235	9	n.a.	n.a.	Koshelkov et al. (1974)
EtOH+*n*-Nonane	760	-0.006	0.83	0.0076	1.08	0.0032	11	n.a.	n.a.	Koshelkov et al. (1974)
EtOH+*n*-Decane	760	-0.006	0.45	0.0037	0.50	0.0024	7	n.a.	n.a.	Koshelkov et al. (1974)
1-PrOH+Benzene	760	-0.097	0.81	0.0294	1.29	0.0262	12	n.a.	n.a.	Prabhu and Van Winkle (1963b)
1-PrOH+*n*-Hexane	760	-0.051	0.82	0.0375	1.62	0.0225	12	n.a.	n.a.	Prabhu and Van Winkle (1963b)
1-PrOH+Cyclohexane	760	-0.055	0.93	0.0269	0.68	0.0128	8	0.69	0.0140	Morachevskii and Chen (1961)
1-PrOH+*n*-Heptane	760	-0.041	0.39	0.0096	0.83	0.0191	9	0.45	0.0237	Gurukul and Raju (1966)
1-PrOH+Toluene	760	-0.093	0.69	0.0254	0.67	0.0059	12	n.a.	n.a.	Lu (1957)

VLE System	P	PPR-3			Wilson		N	Nan et al.		Data Source
	mmHg	δ_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
1-PrOH+Ethylbenzene	760	-0.086	0.94	0.0186	0.47	0.0066	13	0.96	0.0179	Ellis and Froome (1954)
1-PrOH+*p*-Xylene	760	-0.086	0.74	0.0141	0.12	0.0042	25	n.a.	n.a.	Galska-Krajewska (1967)
1-PrOH+*n*-Octane	760	-0.059	1.66	0.0383	1.51	0.0234	13	n.a.	n.a.	Timofeev et al. (1975)
1-PrOH+*n*-Nonane	760	-0.025	1.99	0.0153	1.00	0.0170	12	n.a.	n.a.	Koshelkov et al. (1974)
1-PrOH+*n*-Decane	760	-0.027	1.34	0.0210	1.22	0.0086	12	n.a.	n.a.	Ellis et al. (1960)
2-PrOH+Benzene	760	-0.111	0.37	0.0273	0.40	0.0162	16	0.74	0.0216	Udovenko et al. (1973)
2-PrOH+Cyclohexane	760	-0.050	0.59	0.0298	1.14	0.0363	27	n.a.	n.a.	Yuan et al. (1963)
2-PrOH+*n*-Hexane	760	-0.030	0.47	0.0418	1.07	0.0134	16	n.a.	n.a.	Rotter and Knickle (1977)
2-PrOH+Toluene	760	-0.105	0.97	0.0248	0.45	0.0093	19	n.a.	n.a.	Kireev et al. (1952)
2-PrOH+*n*-Heptane	760	-0.039	0.49	0.0186	0.57	0.0054	26	n.a.	n.a.	Wisniak et al. (1980)
2-PrOH+*n*-Octane	400	-0.034	1.04	0.0330	0.59	0.0181	16	n.a.	n.a.	Prabhu and Van Winkle (1963a)
1-BuOH+Benzene	760	-0.098	0.90	0.0257	0.38	0.0097	18	n.a.	n.a.	Yerazunis et al. (1964)
1-BuOH+Cyclohexane	760	-0.046	1.79	0.0388	0.35	0.0045	27	n.a.	n.a.	Rao and Rao (1963)
1-BuOH+Toluene	760	-0.086	0.38	0.0160	0.19	0.0080	10	n.a.	n.a.	Gorbunov et al. (1968)
1-BuOH+*n*-Heptane	760	-0.035	0.67	0.0175	0.36	0.0046	8	n.a.	n.a.	Hollo and Lengyel (1958)
1-BuOH+Ethylbenzene	760	-0.073	0.51	0.0164	0.16	0.0094	20	n.a.	n.a.	Ellis and Razavipour (1959)
1-BuOH+*p*-Xylene	760	-0.070	0.33	0.0095	0.20	0.0025	17	n.a.	n.a.	Galska-Krajewska (1967)
Tert-BuOH+Benzene	760	-0.140	0.60	0.0196	0.41	0.0041	15	n.a.	n.a.	Govindaswamy et al. (1977)

VLE System	P	PPR-3			Wilson		N	Nan et al.		Data Source
	mmHg	δ_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
Tert-BuOH+Cyclohexane	760	-0.120	1.39	0.0287	2.30	0.0148	18	n.a.	n.a.	Tripathi et al (1976)
Tert-BuOH+*n*-Hexane	760	-0.074	0.75	0.0222	0.49	0.0045	24	n.a.	n.a.	Govindaswamy et al. (1977)
Tert-BuOH+Toluene	760	-0.122	1.22	0.0138	1.15	0.0106	9	n.a.	n.a.	Frolov et al. (1973)
Iso-BuOH+Toluene	760	-0.082	0.29	0.0155	0.37	0.0065	20	n.a.	n.a.	Kireev et al. (1952)
Iso-BuOH+*o*-Xylene	760	-0.070	1.16	0.0235	1.31	0.0088	9	n.a.	n.a.	Chiolan and Cornilescu (1962)
PeOH+Toluene	760	-0.084	0.19	0.0088	0.79	0.0044	13	n.a.	n.a.	Sadler et al. (1971)
PeOH+*p*-Xylene	760	-0.071	0.40	0.0076	0.38	0.0045	19	n.a.	n.a.	Galska-Krajewska (1967)
HeOH+*n*-Hexane	760	-0.089	1.95	0.0251	0.72	0.0376	17	n.a.	n.a.	Rao et al. (1968)
HeOH+*n*-Heptane	760	-0.060	2.44	0.0222	1.52	0.0234	16	1.64	0.0246	Rao et al. (1968)
HeOH+*p*-Xylene	760	-0.071	0.23	0.0097	0.11	0.0032	17	0.87	0.0145	Galska-Krajewska (1967)
HepOH+*n*-Decane	102	-0.030	0.41	0.0239	0.41	0.0055	14	n.a.	n.a.	Cova and Rains (1974)
Overall AAD			0.85	0.0201	0.69	0.0110	712	0.82	0.0182	

Table 5.5: Results of VLE Calculations for Systems involving Two Associating Species under Isobaric Conditions

VLE System	P	PPR-2				PPR-4				Wilson		N	Hong and Hu		Data Source
	mmHg	δ_{AB}	c_{AB}	ΔT/K	Δy	δ_{AB}	c_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
Formic+Acetic	760	-0.024	-20	0.24	0.0323	-0.068	-19	0.61	0.0210	1.43	0.0106	17	0.51	0.0056	Alpert and Elving (1949)
Formic+Propionic	760	-0.022	-20	0.39	0.0472	-0.070	-19	0.68	0.0325	0.80	0.0086	6	0.88	0.0074	Aristovich et al. (1962)
Formic+Butyric	760	-0.032	-20	0.53	0.0660	-0.068	-19	1.79	0.0496	1.96	0.0220	5	0.88	0.0145	Aristovich et al. (1962)
Acetic+Acrylic	760	-0.016	-20	0.53	0.0209	-0.056	-19	0.93	0.0151	0.48	0.0040	16	0.31	0.0047	Chubarov et al. (1976)
Acetic+Propionic	760	-0.007	-19	0.28	0.0319	-0.050	-18	0.37	0.0273	1.90	0.0102	11	1.23	0.0088	Serafimov et al. (1962)
Acetic+Butyric	760	-0.015	-19	0.69	0.0209	-0.040	-19	0.34	0.0181	1.13	0.0046	6	0.54	0.0021	Aristovich et al. (1962)
Acetic+MeOH	760	-0.052	-18	0.55	0.0149	-0.140	-18	1.29	0.0079	1.55	0.0241	19	0.36	0.0060	Sawistowski and Pilavakis (1982)
Acetic+EtOH	760	-0.082	-19	1.35	0.0232	-0.220	-19	1.18	0.0229	2.08	0.0235	16	1.95	0.0037	Amer Amezaga and Fernandez Biarge (1973a)
Acetic+1-PrOH	760	-0.098	-18	1.06	0.0342	-0.200	-19	1.95	0.0440	2.15	0.0159	14	0.35	0.0041	Amer Amezaga and Fernandez Biarge (1973a)
Acetic+2-PrOH	760	-0.110	-20	1.61	0.0397	-0.210	-19	2.46	0.0473	2.56	0.0413	17	1.31	0.0041	Amer Amezaga and Fernandez Biarge (1973b)
Acetic+1-BuOH	706	-0.089	-19	0.44	0.0112	-0.210	-19	1.95	0.0395	0.61	0.0116	20	0.73	0.0056	Rius et al. (1959)
Acetic+2-BuOH	760	-0.102	-20	1.43	0.0297	-0.160	-20	2.41	0.0406	1.47	0.0215	18	n.a.	n.a.	Amer Amezaga and Fernandez Biarge (1973b)
Acetic+Iso-BuOH	760	-0.080	-20	0.92	0.0201	-0.120	-20	1.66	0.0303	0.55	0.0155	23	n.a.	n.a.	Amer Amezaga and Fernandez Biarge (1973b)
Acrylic+1-PrOH	760	-0.072	-20	0.51	0.0259	-0.210	-19	0.82	0.0242	0.64	0.0227	9	0.23	0.0047	Chubarov et al. (1976)
Propionic+1-PrOH	760	-0.071	-20	0.85	0.0340	-0.220	-19	0.86	0.0316	1.63	0.0345	19	n.a.	n.a.	Amer Amezaga (1975a)
Propionic+2-PrOH	760	-0.070	-21	1.47	0.0326	-0.220	-20	1.67	0.0333	2.15	0.0349	18	1.10	0.0057	Amer Amezaga (1975a)

VLE System	P	PPR-2				PPR-4				Wilson		N	Hong and Hu		Data Source
	mmHg	δ_{AB}	c_{AB}	ΔT/K	Δy	δ_{AB}	c_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
Propionic+1-BuOH	760	-0.071	-19	0.74	0.0268	-0.170	-19	1.20	0.0342	0.66	0.0256	17	0.38	0.0042	Amer Amezaga (1975a)
Propionic+2-BuOH	760	-0.080	-21	1.28	0.0339	-0.190	-21	2.07	0.0411	2.19	0.0310	7	0.80	0.0070	Amer Amezaga (1975a)
Propionic+Tert-BuOH	760	-0.100	-22	2.06	0.0339	-0.210	-21	3.08	0.0413	3.05	0.0341	15	1.70	0.0063	Amer Amezaga (1975a)
Propionic+Iso-BuOH	760	-0.067	-21	0.98	0.0319	-0.160	-20	1.50	0.0394	1.31	0.0367	22	0.43	0.0059	Amer Amezaga (1975a)
Propionic+HeOH	760	-0.081	-19	1.08	0.0195	-0.100	-23	2.06	0.0386	1.11	0.0164	18	n.a.	n.a.	Amer Amezaga (1975b)
MeOH+EtOH	760	-0.027	-16	0.23	0.0058	-0.058	-16	0.35	0.0081	0.28	0.0127	14	0.20	0.0125	Amer et al. (1956)
MeOH+1-PrOH	760	-0.037	-16	0.16	0.0110	-0.050	-15	0.50	0.0167	0.92	0.0314	9	0.45	0.0121	Ochi and Kojima (1969)
MeOH+2-PrOH	760	-0.071	-17	0.35	0.0086	-0.103	-16	0.91	0.0172	0.35	0.0088	14	0.45	0.0034	Ochi and Kojima (1969)
MeOH+1-BuOH	760	-0.055	-16	0.78	0.0255	-0.028	-16	1.64	0.0235	1.20	0.0317	9	n.a.	n.a.	Hill and Van Winkle (1952)
MeOH+Iso-BuOH	760	-0.068	-17	0.39	0.0360	-0.050	-19	0.91	0.0471	1.12	0.0421	19	n.a.	n.a.	Ramakrishnan and Sabarethinam (1977)
MeOH+Tert-BuOH	760	-0.111	-17	0.37	0.0084	-0.113	-17	0.97	0.0249	0.40	0.0101	10	0.75	0.0033	Pascal et al. (1921)
MeOH+PeOH	760	-0.070	-20	2.22	0.0326	-0.018	-18	2.47	0.0178	2.06	0.0269	9	2.10	0.0122	Hill and Van Winkle (1952)
MeOH+HeOH	760	-0.100	-18	0.60	n.a.	-0.002	-20	1.00	n.a.	0.11	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
EtOH+1-PrOH	760	-0.010	-15	0.17	0.0059	-0.075	-15	0.42	0.0090	0.22	0.0091	11	n.a.	n.a.	Ochi and Kojima (1969)
EtOH+2-PrOH	760	-0.021	-16	0.07	0.0022	-0.105	-16	0.38	0.0152	0.12	0.0039	13	0.08	0.0024	Ballard and Van Winkle (1952)
EtOH+1-BuOH	760	-0.018	-16	0.32	0.0126	-0.064	-16	1.37	0.0378	0.32	0.0162	9	0.15	0.0023	Hellwig and Van Winkle ((1953)
EtOH+2-BuOH	760	-0.026	-17	0.16	0.0070	-0.082	-17	0.46	0.0137	0.26	0.0044	8	0.28	0.0058	Hellwig and Van Winkle (1953)
EtOH+Iso-BuOH	760	-0.005	-17	0.72	0.0185	-0.055	-17	0.98	0.0338	1.30	0.0192	19	n.a.	n.a.	Andiappan and Mc Lean (1972)
EtOH+Tert-BuOH	760	-0.046	-17	0.10	0.0025	-0.113	-17	0.63	0.0176	0.19	0.0048	13	0.18	0.0021	Suska et al. (1970)
EtOH+PeOH	760	-0.021	-18	1.28	0.0206	-0.066	-17	1.37	0.0279	0.93	0.0175	10	n.a.	n.a.	Hellwig and Van Winkle (1953)

VLE System	P	PPR-2				PPR-4				Wilson		N	Hong and Hu		Data Source
	mmHg	δ_{AB}	c_{AB}	ΔT/K	Δy	δ_{AB}	c_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
EtOH+HeOH	764	-0.034	-20	0.70	n.a.	-0.047	-20	1.08	n.a.	0.12	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
1-PrOH+2-PrOH	760	-0.003	-18	0.14	0.0092	-0.089	-14	0.32	0.0144	1.39	0.0161	29	0.29	0.0044	Ocon et al. (1973)
1-PrOH+1-BuOH	760	-0.004	-16	0.11	0.0022	-0.080	-14	0.27	0.0090	0.07	0.0006	9	0.09	0.0022	Gay (1927)
1-PrOH+Iso-BuOH	760	0.010	-16	0.37	0.0123	-0.072	-15	0.50	0.0166	0.34	0.0088	10	n.a.	n.a.	Mozzhukhin et al. (1967)
1-PrOH+PeOH	755	-0.002	-16	0.11	n.a.	-0.075	-16	0.63	n.a.	0.12	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
1-PrOH+HeOH	765	-0.009	-17	0.16	n.a.	-0.067	-17	0.90	n.a.	0.16	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
2-PrOH+1-BuOH	760	0.008	-15	0.99	0.0091	-0.076	-14	0.64	0.0216	1.12	0.0104	15	1.30	0.0049	Morozov et al. (1978)
2-PrOH+2-BuOH	760	0.009	-15	0.20	0.0080	-0.058	-14	0.24	0.0048	0.35	0.0084	16	0.67	0.0042	Tamir and Wisniak (1975)
2-PrOH+Iso-BuOH	760	0.000	-15	0.17	0.0078	-0.069	-15	0.45	0.0085	0.14	0.0041	9	0.09	0.0021	Ballard and Van Winkle (1952)
2-PrOH+PeOH	758	-0.005	-16	0.35	n.a.	-0.067	-15	0.40	n.a.	0.30	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
2-PrOH+HeOH	761	-0.005	-17	0.13	n.a.	-0.070	-18	0.76	n.a.	0.15	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
1-BuOH+2-BuOH	700	-0.003	-16	0.04	0.0055	-0.080	-15	0.33	0.0072	0.14	0.0044	11	0.06	0.0026	Quitzsch et al. (1969)
1-BuOH+Tert-BuOH	700	-0.013	-16	0.10	0.0084	-0.087	-15	0.31	0.0079	0.50	0.0090	11	n.a.	n.a.	Quitzsch et al. (1969)
1-BuOH+Iso-BuOH	760	0.003	-16	0.07	0.0053	-0.071	-15	0.10	0.0041	0.22	0.0022	17	0.28	0.0035	Tamir and Wisniak (1975)
1-BuOH+HeOH	754	0.003	-17	0.28	n.a.	-0.061	-18	0.53	n.a.	0.30	n.a.	9	n.a.	n.a.	Villa Rivera (1983)
2-BuOH+Iso-BuOH	760	0.002	-16	0.18	0.0056	-0.069	-15	0.13	0.0068	0.22	0.0092	15	0.37	0.0023	Zong et al. (1983)
2-BuOH+Tert-BuOH	760	-0.012	-15	0.27	0.0075	-0.083	-15	0.19	0.0051	0.28	0.0083	20	0.43	0.0048	Wisniak and Tamir (1975)
Iso-BuOH+Tert-BuOH	760	-0.015	-16	0.14	0.0285	-0.081	-15	0.24	0.0325	0.16	0.0427	22	n.a.	n.a.	Wisniak and Tamir (1975)
Formic+Water	760	-0.160	-20	0.82	0.0212	-0.280	-21	1.36	0.0320	0.38	0.0053	17	1.20	0.0195	Chalov and Aleksandrova (1957)
Acetic+Water	760	-0.164	-20	0.87	0.0129	-0.270	-18	0.84	0.0236	0.22	0.0054	13	1.10	0.0078	Shanghai (1976)

VLE System	P	PPR-2				PPR-4				Wilson		N	Hong and Hu		Data Source
	mmHg	δ_{AB}	c_{AB}	ΔT/K	Δy	δ_{AB}	c_{AB}	ΔT/K	Δy	ΔT/K	Δy		ΔT/K	Δy	
Acetic+Acetone	760	-0.015	-21	1.37	0.0077	-0.120	-23	1.12	0.0086	0.98	0.0101	12	n.a.	n.a.	Othmer (1943)
Acetic+Chloroform	760	0.030	-25	1.32	0.0386	-0.075	-22	1.61	0.0169	2.92	0.0300	14	0.75	0.0115	Conti et al. (1960)
MeOH+Water	760	-0.120	-20	0.44	0.0259	-0.200	-21	1.03	0.0282	0.26	0.0116	9	0.82	0.0046	Lesteva et al. (1970)
MeOH+Acetone	775	-0.009	-18	0.21	0.0085	-0.041	-17	0.29	0.0102	0.60	0.0223	11	n.a.	n.a.	Camprell and Kartzmark (1973)
MeOH+Propionaldehyde	755	-0.096	-17	0.24	0.0119	-0.160	-17	1.02	0.0151	0.35	0.0156	19	n.a.	n.a.	Danciu and Dobre (1979)
EtOH+Water	760	-0.140	-19	0.45	0.0165	-0.220	-21	1.00	0.0210	0.12	0.0032	21	0.62	0.0140	Kojima et al. (1968)
EtOH+Acetone	760	0.022	-18	0.15	0.0070	-0.052	-17	0.40	0.0094	0.41	0.0094	6	0.71	0.0063	Aleksandrova and Moiseeva (1971)
EtOH+Acetaldehyde	760	-0.038	-17	1.01	0.0257	-0.080	-15	0.35	0.0175	0.77	0.0185	9	n.a.	n.a.	Heitz (1960)
EtOH+Propionaldehyde	760	-0.004	-16	0.50	0.0122	-0.103	-16	0.63	0.0135	0.66	0.0066	19	n.a.	n.a.	Sundrolm (1964)
EtOH+Chloroform	760	0.036	-19	0.84	0.0192	-0.002	-15	0.87	0.0250	0.38	0.0068	18	n.a.	n.a.	Epnst (1975)
1-PrOH+Acetone	760	0.003	-16	0.43	n.a.	-0.081	-15	0.50	n.a.	0.41	n.a.	10	n.a.	n.a.	Rhim and Kwak (1981)
2-PrOH+Acetone	760	0.040	-15	0.19	0.0068	-0.020	-14	0.19	0.0070	0.31	0.0162	27	n.a.	n.a.	Choffe and Asselineau (1956)
2-PrOH+Chloroform	760	0.028	-16	0.57	0.0157	-0.054	-15	0.59	0.0232	0.90	0.0149	21	n.a.	n.a.	Rao and Rao (1974)
1-BuOH+Acetone	746	0.047	-17	0.47	0.0168	-0.018	-15	0.50	0.0068	0.73	0.0046	15	n.a.	n.a.	Michalski et al. (1961)
1-BuOH+Acetaldehyde	750	-0.108	-15	1.36	0.0075	-0.091	-14	1.80	0.0047	0.61	0.0077	7	n.a.	n.a.	Babakova et al. (1983)
1-BuOH+Chloroform	760	0.020	-20	0.69	0.0613	-0.031	-15	1.72	0.0492	1.18	0.0674	19	n.a.	n.a.	Lepin and Matseevsky (1956)
Tert-BuOH+Acetone	760	0.021	-16	0.24	0.0067	-0.039	-15	0.35	0.0098	0.44	0.0118	15	n.a.	n.a.	Vostrikoya et al. (1974)
Iso-BuOH+Acetone	760	0.030	-16	0.67	0.0301	-0.028	-15	0.62	0.0413	1.21	0.0409	15	n.a.	n.a.	Ramakrishnan and Sabarethinam (1977)
Overall AAD				0.60	0.0195			0.95	0.0226	0.83	0.0170		0.66	0.0061	

Table 5.6: Coefficients of Binary Interaction Parameter δ_{AB}, Equation (5.2.5), for Model PPR-3

System	$\delta_1 \times 10^6 / K^{-2}$	$\delta_2 \times 10^4 / K^{-1}$	δ_3
MeOH+Benzene	-18.93	118.45	-1.92
MeOH+Cyclohexane	0.00	0.00	-0.01
MeOH+*n*-Hexane	-1.20	7.65	-0.12
EtOH+*n*-Butane	0.25	-0.75	-0.05
EtOH+Benzene	-5.48	32.70	-0.56
EtOH+Cyclohexane	-0.76	4.69	-0.10
EtOH+*n*-Hexane	-18.01	114.57	-1.84
EtOH+Toluene	6.57	-41.16	0.57
EtOH+*n*-Heptane	40.46	-261.49	4.19
1-PrOH+Benzene	19.82	-138.00	2.30
1-PrOH+Cyclohexane	17.99	-130.87	2.30
1-PrOH+*n*-Decane	4.93	-82.03	2.00
2-PrOH+Benzene	-10.42	63.16	-1.05
2-PrOH+Cyclohexane	14.20	-93.18	1.47
2-PrOH+*n*-Heptane	6.61	-44.03	0.69
1-BuOH+Benzene	0.00	0.00	-0.07
1-BuOH+Cyclohexane	8.47	-59.82	1.00
1-BuOH+*n*-Hexane	16.00	-95.41	1.38
1-BuOH+Toluene	-40.00	290.52	-5.35
1-BuOH+*n*-Octane	-10.00	74.63	-1.43
1-BuOH+*n*-Decane	0.00	-11.33	0.40
2-BuOH+Benzene	-19.98	127.14	-2.12
Tert-BuOH+Benzene	-15.63	99.45	-1.71
Iso-BuOH+Benzene	-15.04	95.60	-1.60
Iso-BuOH+Toluene	-18.25	128.90	-2.35
PeOH+Toluene	-6.62	45.42	-0.86
PeOH+*n*-Heptane	-22.35	164.58	-3.08
HeOH+*n*-Hexane	2.37	-16.05	0.22
HeOH+Cyclohexane	10.49	-74.32	1.27
DeOH+*n*-Hexane	1.47	-9.50	0.09
DodeOH+*n*-Hexane	10.58	-72.63	1.18

Table 5.7: Coefficients of Binary Interaction Parameter δ_{AB}, Equation (5.2.5), for Models PPR-2 and PPR-4

System	PPR-2		PPR-4	
	$\delta_2 \times 10^4 / K^{-1}$	δ_3	$\delta_2 \times 10^4 / K^{-1}$	δ_3
Acetic+Benzene	3.31	-0.035	4.55	-0.060
Acetic+Cyclohexane	3.07	0	5.04	-0.046
Acetic+*n*-Heptane	9.56	-0.276	5.06	-0.065
Propionic+Cyclohexane	2.26	0.029	4.48	-0.038
Propionic+*n*-Heptane	1.52	0.003	2.99	0

Abbreviation in the Tables of Chapter 5:

Formic	Formic acid
Acetic	Acetic acid
Acrylic	Acrylic acid
Propionic	Propionic acid
Butyric	Butyric acid
Isobutyric	Isobutyric acid
Valeric	Valeric acid
MeOH	Methanol
EtOH	Ethanol
1-PrOH	1-Propanol
2-PrOH	2-Propanol
1-BuOH	1-Butanol
2-BuOH	2-Butanol
Tert-BuOH	Tert-butanol
Iso-BuOH	Iso-butanol
PeOH	Pentanol
HeOH	Hexanol
HepOH	Heptanol
OcOH	Octanol
DeOH	Decanol
DodeOH	Dodecanol

CHAPTER 6
EXPERIMENTAL MEASUREMENT OF EXCESS ENTHALPIES OF BINARY AND TERNARY MIXTURES

Excess molar enthalpy data of binary and ternary mixtures involving alkanol and *n*-alkanes are of importance in industry due to the consequence of the self-association of the alkanols being partially destroyed when they are mixed with inert solvents such as *n*-alkanes. In this work, the excess molar enthalpies of ethanol+*n*-hexane mixtures are measured at 298.15 K, 303.15 K and 313.15 K in an LKB 2107 flow microcalorimeter. The performance and reliability of the microcalorimeter are tested by comparing measured excess molar enthalpies of the ethanol+*n*-hexane mixture at 298.15 K and 303.15 K with those found in the literature. Measurements are also made on a ternary mixture composed of ethanol, *n*-hexane and cyclohexane as well as the three constituent-binary mixtures at 298.15 K.

6.1 Experimental Section

6.1.1 Materials

Ethanol having a purity exceeding 99.98 mol% was supplied by Commercial Alcohols Inc. *n*-Hexane with stated purity exceeding 99 mol% and cyclohexane with purity exceeding 99.9 mol% were purchased from Sigma-Aldrich Co. Apart from partial degassing, all components were used without further purification. Densities of pure ethanol and *n*-hexane in g/cm^3, measured at 298.15 K, 303.15 K and 313.15 K, and cyclohexane, measured at 298.15 K, in an Anton-Paar densimeter (Model DMA38), are listed in Table 6.1 along with the literature values for comparison. The precision of density values is ±0.0001 g·cm^{-3}. These values are in reasonable agreement with values in the literature.

Table 6.1: Densities of Liquids

Component	T/K	ρ_{exp}/ g·cm^{-3}	ρ_{lit}/ g·cm^{-3}	Data Source
Ethanol	298.15	0.7851	0.784931	Hales and Ellender (1976)
	303.15	0.7806	0.780641	Hales and Ellender (1976)
	313.15	0.7725	0.772202	Costello and Bowden (1958a)
n-Hexane	298.15	0.6549	0.654813	Rossini et al. (1953)
	303.15	0.6506	0.650203	Rossini et al. (1953)
	313.15	0.6416	0.641103	Rossini et al. (1953)
Cyclohexane	298.15	0.7733	0.77389	Riddick and Bunger (1970)

6.1.2 Experimental Apparatus and Procedure

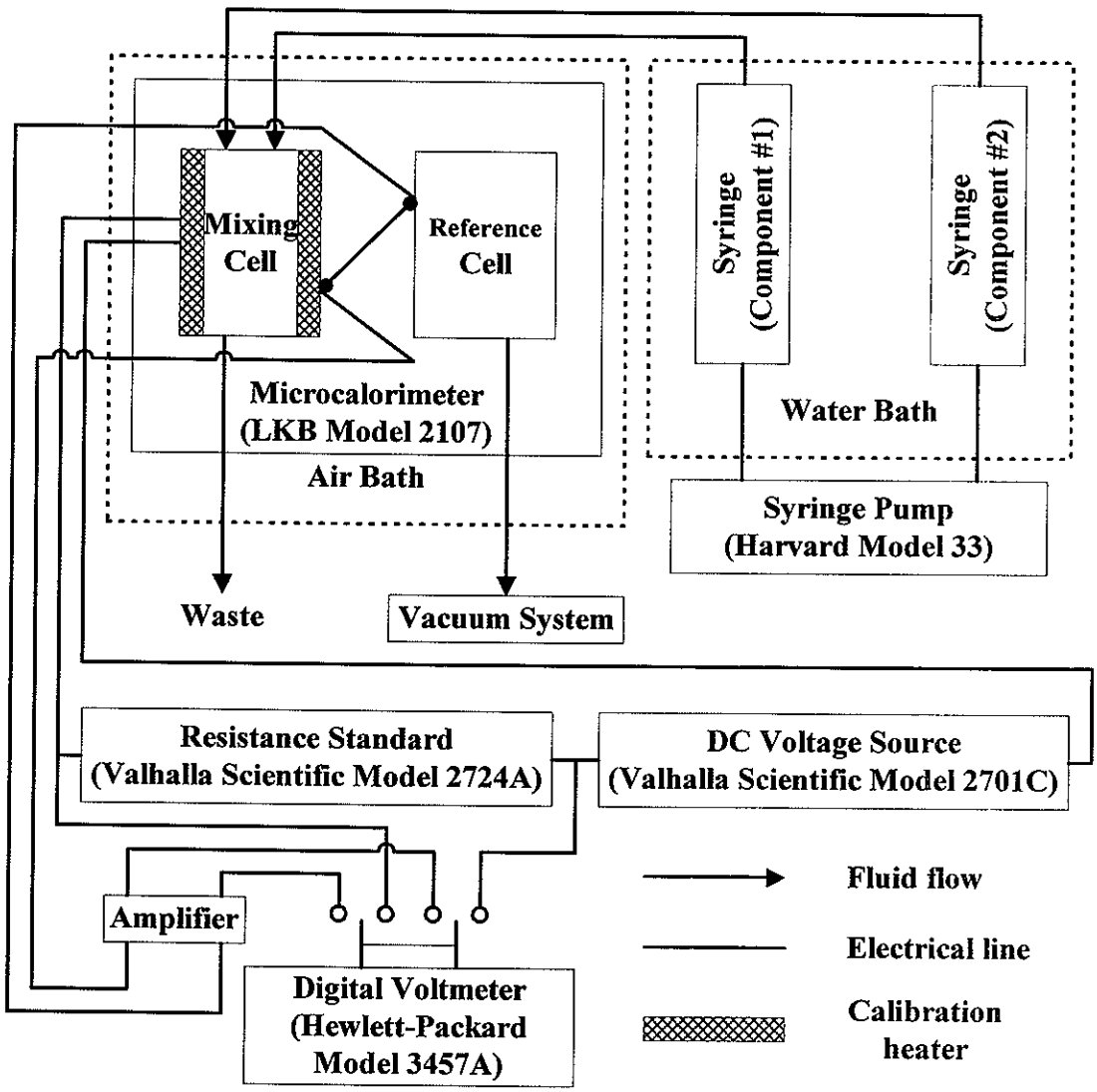

Figure 6.1: Schematic Diagram of Experimental Apparatus

An isothermal microcalorimeter (LKB Model 2107) apparatus and the required fluids displacement mechanism are used for measuring the excess molar enthalpies of mixtures in this work. A schematic diagram of the experimental setup is shown in Figure 6.1. The principles on which the measurements are based, and the operating procedure, are essentially identical to those described by Tanaka *et al.* (1975) for binary mixtures. In the present work, the calorimeter unit is placed in a temperature-controlled air bath, augmented by a cooling water system. The temperature in the air bath is measured by means of a precision digital thermometer (Azonix Model A1011 equipped with a CT41 platinum resistance probe) with a precision of 0.001°C and an accuracy of ±0.005°C. The temperature control is quite stable as the temperature measurements of the air bath over a 15-hour period show less than a 0.005°C variation under the experimental conditions. A syringe pump (Harvard Apparatus Model 33), placed vertically in order to minimize the possibility of generating gas bubbles in the flow lines, is used to deliver the working liquids at selected volumetric flow rates into the mixing cell of the microcalorimeter. The description of the calibration and the calibration results for a syringe pump are presented in Appendix E and Tables E1 and E2, respectively. A precision direct current voltage source (Valhalla Scientific Model 2701C) is used with a programmable resistance standard (Valhalla Scientific Model 2724A) to provide the calibration current for the calorimeter heater circuit. The calibration constant for a pure liquid is obtained from the heat effects generated from the difference between the thermopile output taken with applying an electric current input to the calorimeter heater and the one without applying an electrical current to the heater over a range of flow rates. The detailed description and the results of the calibration constant for three pure liquids are given in Appendix E. The calibration constants determined for the liquids and the volume fractions of the components are used to convert the amplified thermoelectric output displayed on a digital voltmeter (Hewlett-Packard Model 3457A Multimeter) to the excess molar enthalpies of the mixture. The values of the excess molar enthalpies of the mixture are calculated from the following expression:

$$H^E = \frac{\varepsilon_M(f,t)\left[E_M(f) - E_M^0(f)\right]}{f_1/V_1 + f_2/V_2} \qquad (6.1.2.1)$$

where V_i is the molar volume of component *i*. The voltage readings, E_M, obtained from

a digital voltmeter (Hewlett-Packard Model 3457A Multimeter) are taken for a number of mixtures in which the mole fraction of one component ranges from 0 to 1. The baseline voltage for a mixture E_M^0, is the volumetric average of the baseline voltages for the pure liquids at the same flow-rate. It can be expressed as

$$E_M^0(f) = \phi_1 E_1^0(f) + \phi_2 E_2^0(f) \qquad (6.1.2.2)$$

where ϕ_i is the volume fraction of component *i*, which is defined as $\phi_i = f_i / \sum_i f_i$. f_i refers to the volume flow rate of component *i*. The term f in Equation (6.1.2.2) is the total volume flow rate of a mixture and it is taken to have a value of 18 ml·h^{-1} in terms of the specification of the microcalorimeter. $E_1^0(f)$ and $E_2^0(f)$ are the baseline voltages of components 1 and 2 at 18 ml·h^{-1} flow rate, respectively. The approximate expression (Tanaka *et al.*, 1975) for the calibration constant of a mixture, $\varepsilon_M(f,t)$ is given by

$$\varepsilon_M(f,t) = \phi_1 \varepsilon_1(f,t) + \phi_2 \varepsilon_2(f,t) \qquad (6.1.2.3)$$

where $\varepsilon_1(f,t)$ and $\varepsilon_2(f,t)$ are the calibration constants of components 1 and 2 at temperature *t*, respectively.

Using different ratios of volumetric flow rates of component 1 and 2, a wide range of liquid compositions can be investigated experimentally. The corresponding values of the excess molar enthalpy can be obtained from Equation (6.1.2.1). The overall uncertainties in the excess molar enthalpy values due to the systematic errors in both flow rates and voltage readings are estimated to be less than 0.5% over most of the mole fraction range except for the dilute region of component 1 and 2.

Following the procedure mentioned above, one can measure the excess molar enthalpy data of binary mixtures. In studying the excess molar enthalpies of a ternary mixture (say, components 1+2+3), the excess molar enthalpy, which is designated as $H_{m,1+23}^E$, is determined for several pseudo-binary mixtures in which component 1 is added to the binary systems of components 2 and 3 having fixed compositions. For this purpose, three mixtures of the binary system (2+3) are prepared. The mole fractions of component 2 in the three binaries are 0.25, 0.5 and 0.75, respectively. The preparation of each of these mixtures is accomplished by means of weighing the appropriate amounts of the degassed constituent pure samples and mixing them in a glass flask. The

temperature, barometric pressure and humidity are recorded to correct the weight measurements to weight in a vacuum. The excess molar enthalpy $H^E_{m,123}$ of a ternary mixture is obtained from the following equation:

$$H^E_{m,123}/(\text{J/mol}) = H^E_{m,1+23} + (1-x_1)H^E_{m,23} \qquad (6.1.2.4)$$

where $H^E_{m,23}$ is the excess molar enthalpy of the particular binary mixture. The errors of $H^E_{m,1+23}$ are estimated to be less than 0.5% over most of the mole fraction range of component 1.

6.1.3 Results and Discussion

6.1.3.1 Binary Mixtures

The experimental excess molar enthalpy values of ethanol+*n*-hexane mixtures at 25°C, 30°C and 40°C are summarized in Table 6.2. The experimental data of ethanol+cyclohexane and *n*-hexane+cyclohexane mixtures at 25°C are summarized in Table 6.3. The excess molar enthalpy values can be represented by the following smoothing function (Wang *et al.*, 1992):

$$H^E_{m,ij}/(\text{J/mol}) = x_i(1-x_i)\left[1+A_0(1-2x_i)\right]^{-1}\sum_{p=1}^{n}A_p(1-2x_i)^{p-1} \qquad (6.1.3.1.1)$$

The coefficients A_0 and A_p ($P \geq 1$), which are determined by a least-squares method, are listed in Table 6.4 along with the standard error s of the fitting for the binary mixtures. The standard error is defined as

$$s = \sqrt{\frac{\sum(H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{cal}})^2}{N-n}} \qquad (6.1.3.1.2)$$

where $H^{\mathrm{E}}_{\mathrm{exp}}$ and $H^{\mathrm{E}}_{\mathrm{cal}}$ stand for the experimental and calculated excess molar enthalpy values, respectively; N refers to the number of the experimental data. For each set of data, the appropriate number n of the coefficients, A_p, in Equation (6.1.3.1.1) is determined by making the variation of the standard error minimized. The experimental data and the fitting by use of Equation (6.1.3.1.1) for three constituent-binary mixtures along with the literature values are plotted in Figures 6.2 - 6.5. It can be seen that the excess molar enthalpy data are positive over the entire mole fraction range and the

experimental results can be very accurately represented by the smoothing equation with appropriate coefficients.

Table 6.2: Experimental Results for the Excess Molar Enthalpies $H^E_{m,12}$ of Ethanol(1)+*n*-Hexane(2) System at 298.15 K, 303.15 K and 313.15 K

x_1	$H^E_{m,12}$ / J·mol^{-1}	x_1	$H^E_{m,12}$ / J·mol^{-1}	x_1	$H^E_{m,12}$ / J·mol^{-1}
298.15 K		303.15 K		313.15 K	
0.050	343.5	0.030	330.6	0.040	507.9
0.100	423.3	0.050	399.4	0.050	541.7
0.150	477.3	0.100	474.1	0.075	589.6
0.200	521.3	0.150	533.9	0.100	630.9
0.250	547.7	0.200	576.7	0.150	718.8
0.300	557.9	0.250	610.5	0.200	770.1
0.350	571.9	0.300	637.0	0.250	808.3
0.400	576.7	0.350	648.1	0.300	837.0
0.450	572.2	0.400	644.2	0.350	842.2
0.500	567.8	0.450	634.2	0.400	828.6
0.550	540.8	0.500	618.7	0.450	813.2
0.600	507.1	0.550	592.6	0.500	778.4
0.650	477.9	0.600	563.2	0.550	743.1
0.700	444.1	0.650	531.4	0.600	696.5
0.750	399.6	0.700	486.0	0.650	654.1
0.800	346.8	0.750	433.9	0.700	588.9
0.850	284.0	0.800	377.2	0.750	520.5
0.900	207.9	0.850	304.1	0.800	447.4
0.950	114.3	0.900	227.8	0.850	362.8
		0.950	125.6	0.900	259.6
				0.950	145.6

The excess molar enthalpies of the ethanol+*n*-hexane mixture at 25°C and 30°C obtained in this work have been used to investigate the reliability of the microcalorimeter by comparing the measured data with the values available from the literature. Figure 6.3 serves to indicate the good agreement of our results with the experimental data of Wang *et al.* (1992), who used an LKB 10070 flow microcalorimeter to measure the excess molar enthalpies of the ethanol+*n*-hexane mixture at 25°C. The results from Bykov (1939), who used a batch twin titration calorimeter, are more scattered than ours and cover a narrower concentration range than all the other sets of data. In the case of the data for the ethanol+*n*-hexane mixture at

30°C, the experimental results reported by Savini *et al.* (1965) are close to the results of this work. Their curve indicates the maximum value of $H_m^E(0.4) = 629$ J·mol^{-1}, which is 16 J·mol^{-1} smaller than the 645 J·mol^{-1} obtained from our curve.

Table 6.3: Experimental Results for the Excess Molar Enthalpies $H_{m,13}^E$ and $H_{m,23}^E$ of Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15 K

x_1	$H_{m,13}^E$ / J·mol^{-1}	x_2	$H_{m,23}^E$ / J·mol^{-1}
0.050	319.1	0.050	59.4
0.100	424.0	0.100	104.0
0.150	498.9	0.150	143.1
0.200	547.9	0.200	170.7
0.250	584.2	0.250	192.3
0.300	606.2	0.300	207.7
0.350	627.9	0.350	217.3
0.400	635.8	0.400	220.7
0.450	635.7	0.450	219.8
0.500	631.5	0.500	216.8
0.550	614.7	0.550	208.8
0.600	590.0	0.600	195.4
0.650	557.3	0.650	180.3
0.700	522.4	0.700	164.0
0.750	470.8	0.750	140.9
0.800	410.6	0.800	118.1
0.850	335.5	0.850	92.5
0.900	244.0	0.900	65.8
0.950	137.7	0.950	35.3

Table 6.4: Coefficients A_0, A_p of Equation (6.1.3.1.1) and the Standard Error s for the Fitting of $H_{m,ij}^E$ for Appropriate Binary Mixtures of System Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3)

Component i	Component j	T K	A_0	A_1	A_2	A_3	A_4	A_5	s J·mol^{-1}
Ethanol	*n*-Hexane	298.15	-0.9631	2234.65	-1494.07	263.49	-597.08	447.39	3.91
Ethanol	*n*-Hexane	303.15	-0.9738	2480.25	-1580.41	157.05	-756.25	594.22	3.09
Ethanol	*n*-Hexane	313.15	-0.9984	3129.68	-1768.28	72.30	-965.08	381.95	3.91
Ethanol	Cyclohexane	298.15	-0.9700	2510.46	-2001.44	658.49	-533.64		2.48
n-Hexane	Cyclohexane	298.15	-3.0585	863.33	-2368.95	-708.31	-372.88		1.09

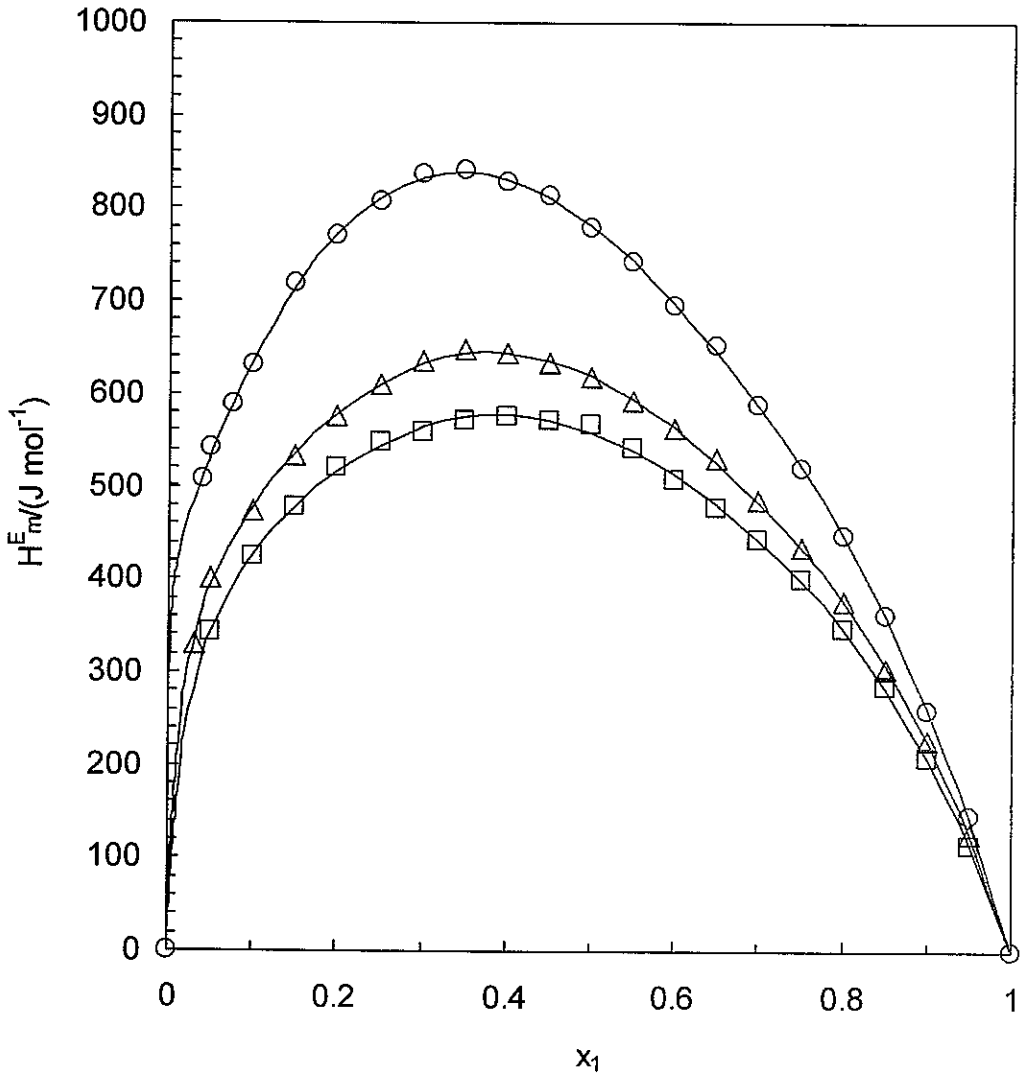

Figure 6.2: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at Different Temperatures. Experimental Results: □, 298.15 K; Δ, 303.15 K; o, 313.15 K; —, Calculated from Equation (6.1.3.1.1) with Coefficients from Table 6.4.

The experimental excess molar enthalpies of ethanol+cyclohexane and *n*-hexane+cyclohexane mixtures at 25°C have been compared with literature values as well. It can be seen from Figure 6.4 that for an equimolar mixture of ethanol+cyclohexane at 25°C, the excess molar enthalpy values reported by Nagata and Kazuma (1977) are about 633 J·mol^{-1}, which is slightly larger than the 631.5 J·mol^{-1} obtained from our curve. Marsh (1973) and Tanaka *et al.* (1975) reported the excess

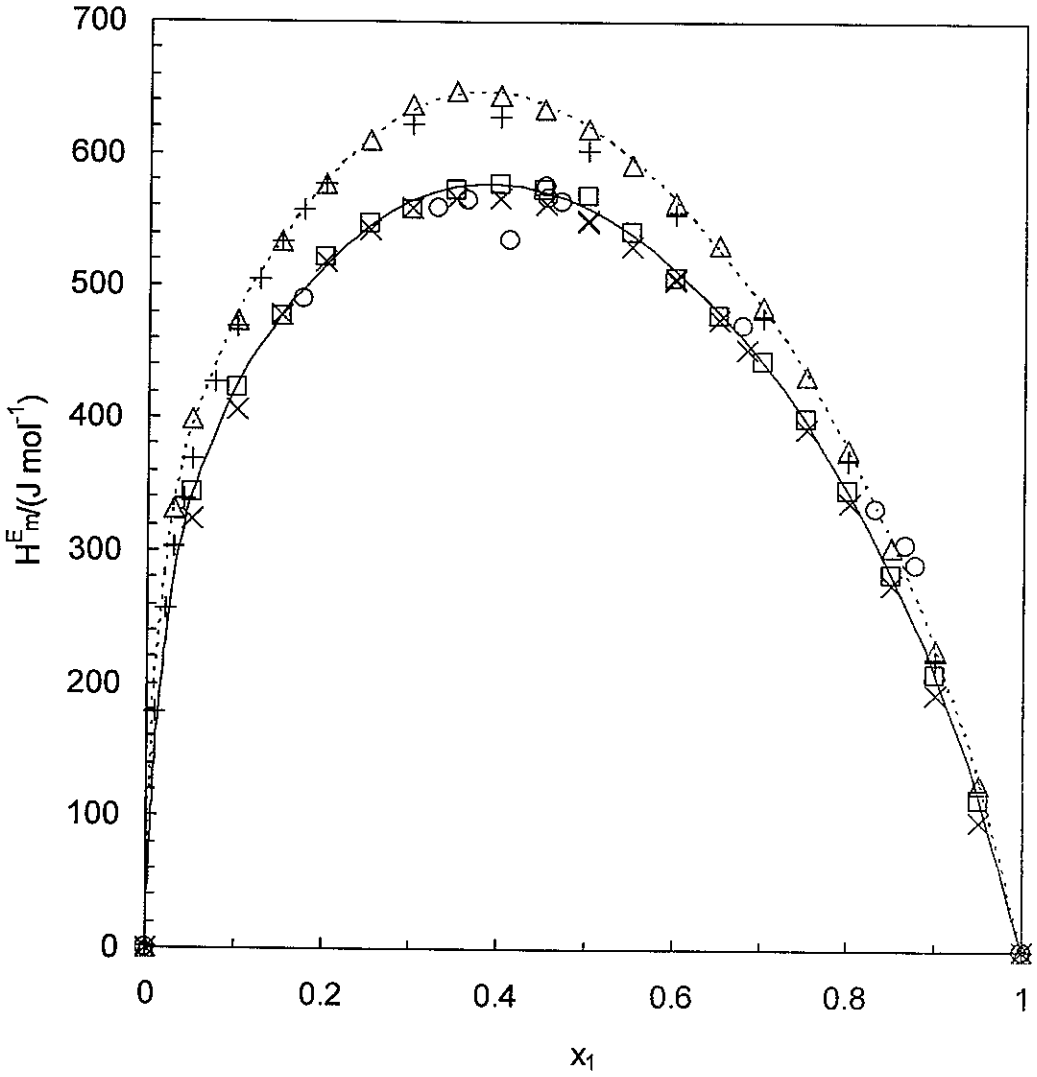

Figure 6.3: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at 298.15 K and 303.15 K. Experimental Results at 298.15 K: □, this work; ×, Wang *et al.* (1992); o, Bykov (1939); —, Calculated from Equation (6.1.3.1.1) with Coefficients from Table 6.4 at 298.15 K. Experimental Results at 303.15 K: Δ, this work; +, Savini *et al.* (1965); ----, Calculated from Equation (6.1.3.1.1) with Coefficients from Table 6.4 at 303.15 K.

molar enthalpies for *n*-hexane+cyclohexane mixture at 25°C. Figure 6.5 presents the comparison of our results with the experimental data of Tanaka *et al.* (1975), which are very close to the results of this work. It appears that the excess molar enthalpies at cyclohexane-rich region are slightly larger than the literature values measured by Marsh (1973). The maximum value of excess molar enthalpy is 220 J·mol^{-1} from this work,

which is 1 J·mol^{-1} smaller than the 221 J·mol^{-1} reported by Marsh (1973) and 0.2 J·mol^{-1} larger than the 219.8 J·mol^{-1} reported by Tanaka *et al.* (1975) near $x_2 = 0.4$.

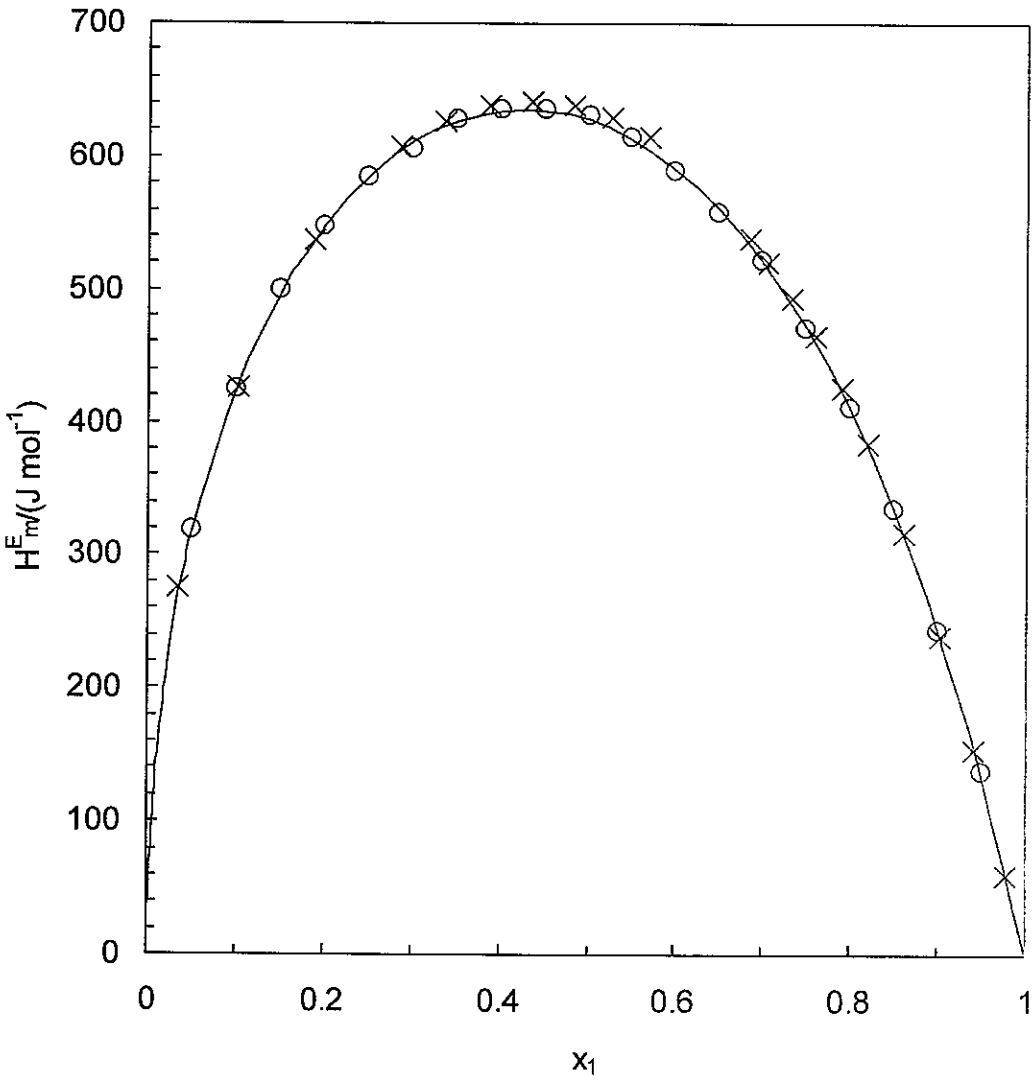

Figure 6.4: Excess Molar Enthalpies for Ethanol(1)+Cyclohexane(3) System at 298.15 K. Experimental Results: o, this work; ×, Nagata and Kazuma (1977); —, Calculated from Equation (6.1.3.1.1) with Coefficients from Table 6.4.

6.1.3.2 Ternary Mixtures

The experimental values of $H^E_{m,1+23}$ measured in this work and the corresponding values of $H^E_{m,123}$ for ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture are listed in Table

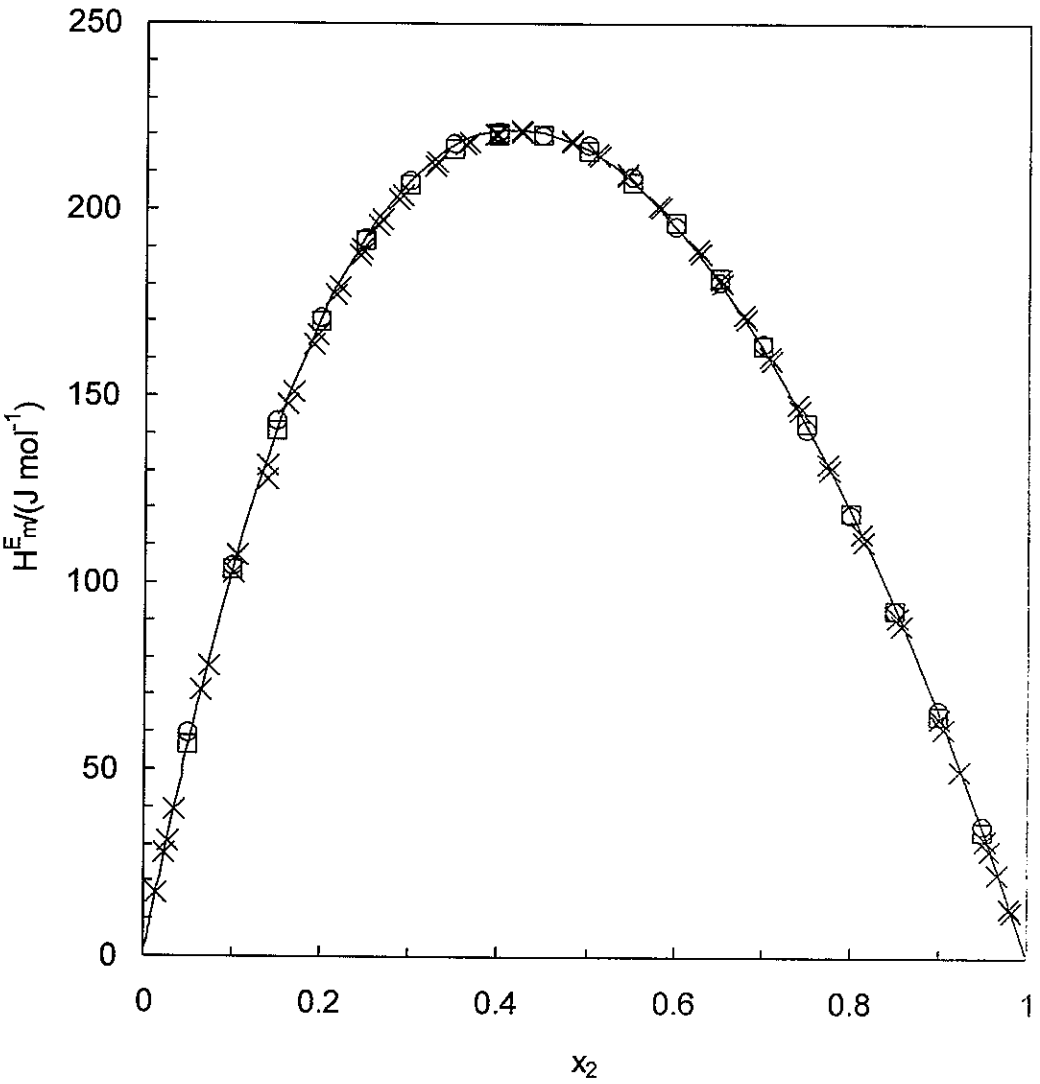

Figure 6.5: Excess Molar Enthalpies for *n*-Hexane(2)+Cyclohexane(3) System at 298.15 K. Experimental Results: o, this work; ×, Marsh (1973); □, Tanaka *et al.* (1975); —, Calculated from Equation (6.1.3.1.1) with Coefficients from Table 6.4.

6.5. Plots of $H^E_{m,1+23}$ against the mole fraction x_1 of ethanol are given in Figure 6.6. Also included in this figure are the smooth representations of the excess molar enthalpies of the constituent-binary mixtures corresponding to the cases $x_2 = 0$ and $x_3 = 0$, which are calculated from Equation (6.1.3.1.1) using the coefficients in Table 6.4. The maximum value of $H^E_{m,1+23}$ occurs near $x_1 = 0.4$ and at the constant value of x_1, $H^E_{m,1+23}$ increases

Table 6.5: Experimental Results for the Excess Molar Enthalpies $H^E_{m,1+23}$ at 298.15 K for the Addition of Ethanol to *n*-Hexane+Cyclohexane Mixtures to Form Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3), and Values of $H^E_{m,123}$ Calculated from Equation (6.1.2.4) Using the Smooth Representation of $H^E_{m,23}$ by Equation (6.1.3.1.1)

x_1	$H^E_{m,1+23}$ [a] J·mol^{-1}	$H^E_{m,123}$ J·mol^{-1}	x_1	$H^E_{m,1+23}$ J·mol^{-1}	$H^E_{m,123}$ J·mol^{-1}	x_1	$H^E_{m,1+23}$ J·mol^{-1}	$H^E_{m,123}$ J·mol^{-1}
		$x_2/(1-x_1-x_2) = 0.3338$, $H^E_{m,23}$ / J mol^{-1} = 193.1						
0.050	323.70	507.16	0.400	584.96	700.83	0.700	470.86	528.80
0.100	417.72	591.53	0.450	582.73	688.94	0.750	424.81	473.09
0.150	479.06	643.21	0.500	572.50	669.06	0.800	369.07	407.70
0.200	522.98	677.47	0.550	556.24	643.14	0.850	302.84	331.81
0.250	549.34	694.18	0.600	534.50	611.75	0.900	220.88	240.19
0.300	570.42	705.60	0.650	506.30	573.89	0.950	120.77	130.43
0.350	580.41	705.93						
		$x_2/(1-x_1-x_2) = 0.9989$, $H^E_{m,23}$ / J mol^{-1} = 215.9						
0.050	326.46	531.53	0.400	571.55	701.07	0.700	451.58	516.34
0.100	417.44	611.72	0.450	565.06	683.79	0.750	408.28	462.25
0.150	471.05	654.54	0.500	554.53	662.46	0.800	355.88	399.05
0.200	513.22	685.91	0.550	538.04	635.18	0.850	292.33	324.71
0.250	540.06	701.97	0.600	516.23	602.58	0.900	212.46	234.05
0.300	559.23	710.34	0.650	487.03	562.58	0.950	117.14	127.93
0.350	569.59	709.91						
		$x_2/(1-x_1-x_2) = 2.9752$, $H^E_{m,23}$ / J mol^{-1} = 142.8						
0.050	331.30	466.97	0.400	565.29	650.97	0.700	442.92	485.76
0.100	414.35	542.88	0.450	560.46	639.01	0.750	401.04	436.74
0.150	466.45	587.84	0.500	550.13	621.54	0.800	347.79	376.35
0.200	504.56	618.81	0.550	533.34	597.60	0.850	284.56	305.98
0.250	531.54	638.65	0.600	510.82	567.94	0.900	209.01	223.29
0.300	550.37	650.33	0.650	479.35	529.33	0.950	115.33	122.47
0.350	562.06	654.89						

[a] Ternary term for representation of $H^E_{m,1+23}$ by Equations (6.1.3.2.1) and (6.1.3.2.2):

$$H^E_{m,T}/(\text{J/mol}) = [x_1x_2x_3/(1-x_1+x_2)](-838.95 - 2998.30x_1 + 3887.42x_2$$

$$+ 5133.45x_1^2 - 1445.65x_1x_2 - 5762.50x_2^2 - 2256.68x_1^3) \quad s = 0.92 \text{ J·mol}^{-1}$$

with increase in the relative content of the cyclohexane in the mixture. It is interesting to note that there is a perceptible crossing of the curves for this ternary mixture at a low

mole fraction of ethanol ($x_1 < 0.05$). This behavior is similar to the one found in the literature (Peng *et al.*, 1998; Zhu *et al.*, 1993) for mixtures containing ethanol. The values of $H^E_{m,1+23}$ can be represented as a sum of binary terms with an added ternary correction:

$$H^E_{m,1+23}/(\text{J/mol}) = \frac{x_2}{(1-x_1)} H^E_{m,12} + \frac{(1-x_1-x_2)}{(1-x_1)} H^E_{m,13} + H^E_{m,T} \qquad (6.1.3.2.1)$$

where the $H^E_{m,ij}$ values are calculated from the appropriate smoothing function in Equation (6.1.3.1.1). The form of ternary contribution in Equation (6.1.3.2.1) is given by

$$H^E_{m,T}/(\text{J/mol}) = \frac{x_1 x_2 (1-x_1-x_2)}{(1-x_1+x_2)} (c_0 + c_1 x_1 + c_2 x_2 + c_3 x_1^2 + c_4 x_1 x_2 + c_5 x_2^2 + \ldots) \qquad (6.1.3.2.2)$$

Equation (6.1.3.2.2) is similar to the form used by Morris *et al.* (1975). The coefficient values c_i are obtained from the least-squares analyses, in which Equations (6.1.3.2.1) and (6.1.3.2.2) are fitted to the experimental values of $H^E_{m,1+23}$ in Table 6.5. The resulting representation of $H^E_{m,T}$ is given in the footnote of the table where the standard deviation of the representation is also indicated. The solid curves in Figure 6.6 are calculated from Equation (6.1.3.2.1) using this representation.

Equations (6.1.2.4), (6.1.3.1.1), (6.1.3.2.1) and (6.1.3.2.2) are also used to calculate the constant $H^E_{m,123}$ contours plotted on the Roozeboom diagrams in Figure 6.7. It can be seen that some of the contours do not extend to the edges of the triangle, but indicate a rise of $H^E_{m,123}$ to an internal maximum near the centroid of the triangle. This corresponds to the value of $H^E_{m,123}$ equal to 711 J·mol^{-1}.

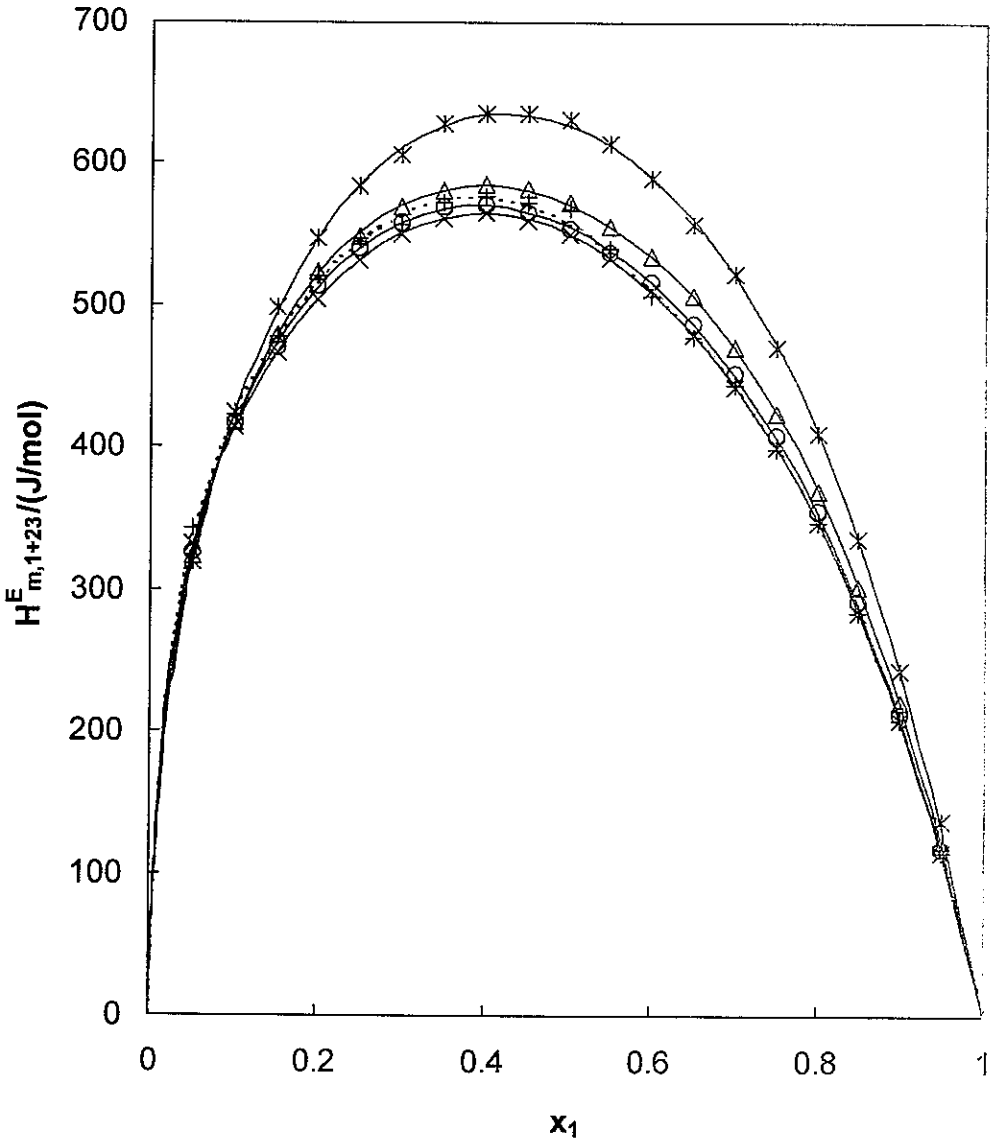

Figure 6.6: Excess Molar Enthalpies $H^E_{m,1+23}$ for Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15K Plotted against Mole Fraction x_1. Experimental Results: Δ, $x_2/(1-x_1-x_2)=0.3338$; o, $x_2/(1-x_1-x_2)=0.9989$; ×, $x_2/(1-x_1-x_2)=2.9752$; *, $x_2=0$; +, $x_3=0$. Curves: ---, $x_3=0$; —, Calculated from the Representation of the Results by Equations (6.1.3.2.1) and (6.1.3.2.2) using the Ternary Term $H^E_{m,T}$ given in the Footnote of Table 6.5.

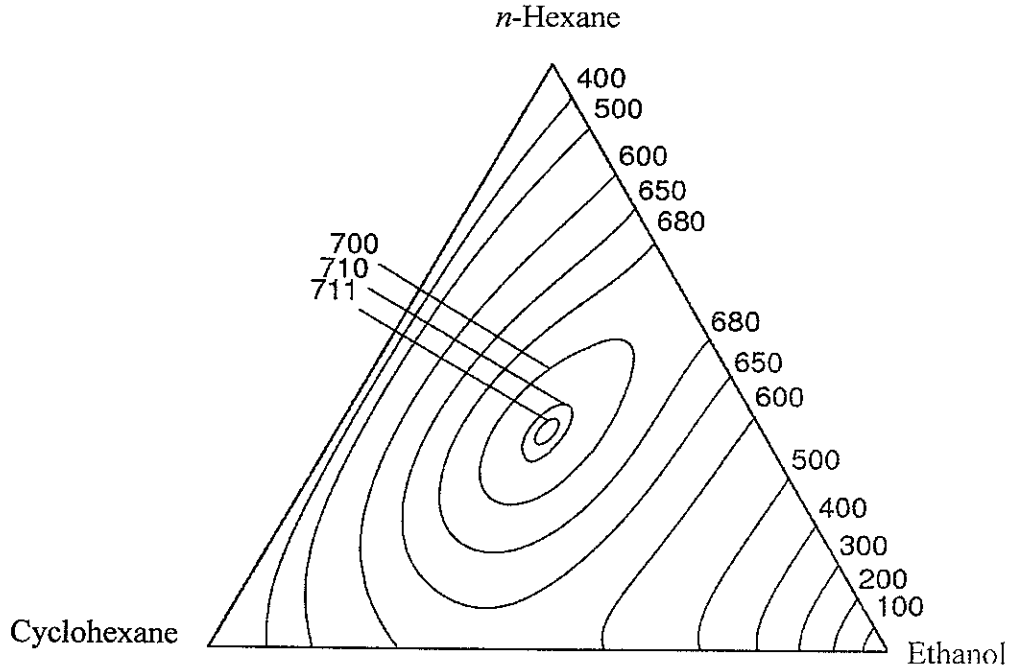

Figure 6.7: Contours for Constant Values of $H^{E}_{m,123}$/J·mol^{-1} for Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15 K Obtained from the Representation of the Experimental Results by Equations (6.1.2.4), (6.1.3.1.1), (6.1.3.2.1) and (6.1.3.2.2) with $H^{E}_{m,T}$ from the Footnote of Table 6.5.

6.2 Calculations from Different Models

6.2.1 Liebermann-Fried Model

The Liebermann-Fried model (Liebermann and Fried, 1972a, 1972b) has the ability to correlate the excess molar enthalpy of binary mixtures. Details of the thermodynamic relations in connection with the derivation of the Liebermann-Fried model were described by Wang and Lu (2000). To facilitate the understanding of the application of the Liebermann-Fried model, we present only the equations used in the calculation process.

The expression for H^{E} of binary mixtures has the following form:

$$H^E = \frac{\beta RTx_1x_2\left[\ln(A_{12}A_{21})\right]^2}{(x_1+x_2A_{12})(x_2+x_1A_{21})\left[2-\ln(A_{12}A_{21})\right]}\left[\frac{x_2A_{12}}{x_1+x_2A_{12}}+\frac{x_1A_{21}}{x_2+x_1A_{21}}-\frac{2}{\ln(A_{12}A_{21})}\right]$$

$$+RT^2\left[\frac{x_1(\partial V_1/\partial T)+x_2(\partial V_2/\partial T)}{x_1V_1+x_2V_2}-\frac{x_1(\partial V_1/\partial T)}{V_1}-\frac{x_2(\partial V_2/\partial T)}{V_2}\right] \quad (6.2.1.1)$$

Wang and Lu (2000) neglected the dependence of molar volumes on temperature and found that it was appropriate to set the value of the adjustable parameter β equal to 2 (Liebermann and Fried, 1972a). Thus, Equation (6.2.1.1) can be simplified to

$$H^E = \frac{2RTx_1x_2\left[\ln(A_{12}A_{21})\right]^2}{(x_1+x_2A_{12})(x_2+x_1A_{21})\left[2-\ln(A_{12}A_{21})\right]}$$

$$\times\left[\frac{x_2A_{12}}{x_1+x_2A_{12}}+\frac{x_1A_{21}}{x_2+x_1A_{21}}-\frac{2}{\ln(A_{12}A_{21})}\right] \quad (6.2.1.2)$$

In the work of Peng *et al.* (2001), the derivatives of molar volumes with respect to temperature were calculated in terms of the modified Rackett equation (Rackett, 1970; Spencer and Danner, 1972) in the following form:

$$V = \frac{RT_C}{P_C}Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]} \quad (6.2.1.3)$$

where P_C, T_C and Z_{RA} are the critical pressure, critical temperature and reference compressibility factor of pure substances. Table 6.6 lists the parameter values of pure substances used in this work.

Table 6.6: Parameters for Pure Substances

Substance	T_C/K	P_C/MPa	Z_{RA}
Ethanol	516.25	6.3835	0.2480
n-Hexane	507.43	3.0120	0.2635
Cyclohexane	553.54	4.0700	0.2729

In this work, Equations (6.2.1.1) and (6.2.1.2) are used to estimate the excess molar enthalpies of binary mixtures. The values of the binary parameters A_{12} and A_{21} for the ethanol(1)+*n*-hexane(2) mixture at 298.15 K, 303.15 K and 313.15 K are determined by fitting the Liebermann-Fried formula to the experimental data of the excess molar enthalpy. The parameters are presented in Table 6.7 along with the relative

root mean square (RRMS) errors defined as

$$RRMS = \sqrt{\frac{1}{N-p}\sum_{i=1}^{N}\left(\frac{H^{E}_{expt,i} - H^{E}_{calc,i}}{H^{E}_{expt,i}}\right)^{2}} \times 100 \qquad (6.2.1.4)$$

Table 6.7: Values of the Parameters A_{12} and A_{21}, Relative Root Mean Square (RRMS) Errors in Liebermann-Fried Model Calculations for Ethanol(1)+*n*-Hexane(2) Mixture at 298.15 K, 303.15 K and 313.15 K

T	Equation (6.2.1.1)			Equation (6.2.1.2)		
K	A_{12}	A_{21}	RRMS	A_{12}	A_{21}	RRMS
298.15	0.4887	1.3434	18.240	0.4889	1.3426	18.246
303.15	0.4411	1.4327	22.456	0.4414	1.4316	22.463
313.15	0.3472	1.6409	20.608	0.3475	1.6394	20.622

where N is the number of observed data and p represents the appropriate number of adjustable coefficients and is equal to 2 for binary mixtures. It can be concluded from Table 6.7 that there is no significant improvement by considering the dependence of molar volumes on temperature. Either Equation (6.2.1.1) or Equation (6.2.1.2) can be used to calculate the excess molar enthalpies of binary mixtures. The calculated results obtained from Equation (6.2.1.1) and the experimental data for the ethanol(1)+*n*-hexane(2) mixture at three temperatures are shown in Figure 6.8 for comparison. It can be seen that the calculated results based on the Liebermann-Fried model are larger than the experimental data over the mole fraction range $0.2 < x_1 < 0.6$ whereas the calculated values are smaller than the experimental data over the mole fraction range $x_1 < 0.2$ and $x_1 > 0.6$ for the ethanol(1)+*n*-hexane(2) mixture at 298.15 K. Similar trends are evident at 303.15 K and 313.15 K for the ethanol(1)+*n*-hexane(2) mixture as well.

The values of A_{12} and A_{21} for the ethanol(1)+cyclohexane(3) and *n*-hexane(2)+cyclohexane(3) mixtures at 298.15 K are given in Table 6.8. Also included in this table are the values of the errors achieved in the fitting process. The comparisons of the calculated values obtained from Equation (6.2.1.1) for the ethanol(1)+cyclohexane(3) and *n*-hexane(2)+cyclohexane(3) mixtures are illustrated in Figures 6.9 and 6.10, respectively. The values of excess molar enthalpy for ethanol(1)+*n*-hexane(2) and ethanol(1)+cyclohexane(3) mixtures yield curves which are

skewed towards low ethanol mole fraction. It is clear that the Liebermann-Fried model is capable of representing the excess molar enthalpies of the *n*-hexane(2)+cyclohexane(3) mixture which involves only non-associating substances with better accuracy than those of ethanol(1)+*n*-hexane(2) and ethanol(1)+cyclohexane(3) mixtures which contain one associating substance as compared with the corresponding experimental data from this work.

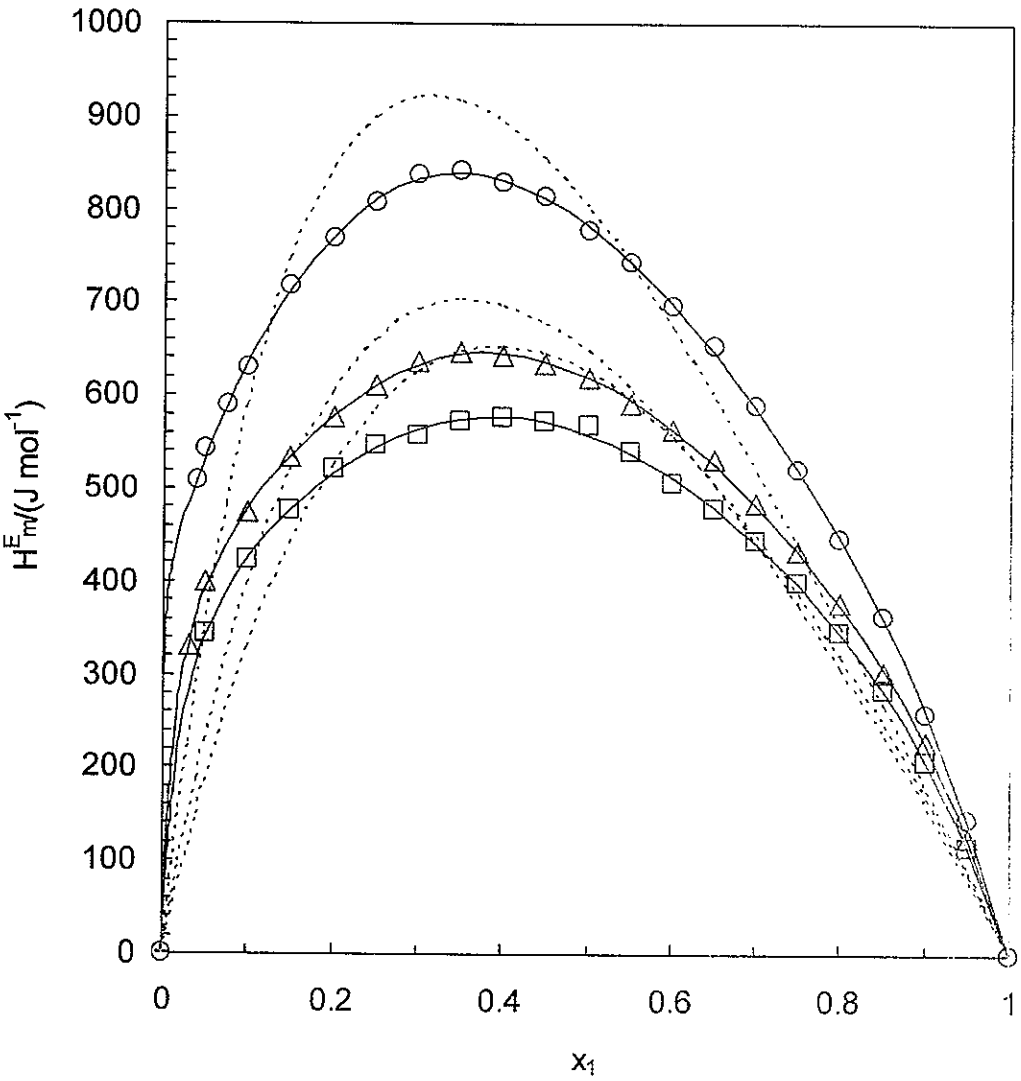

Figure 6.8: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at Different Temperatures. Experimental Results: □, 298.15 K; Δ, 303.15 K; o, 313.15 K; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from Liebermann-Fried Model Equation (6.2.1.1).

The Liebermann-Fried model can be extended to estimate the excess molar enthalpies of ternary mixtures (Peng *et al.*, 2001). The expression of $H^E_{m,123}$ is represented in the following form:

$$H^E_{m,123} = \frac{RT^2}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}\frac{x_j x_k\left[\frac{dA_{jk}}{dT}+\frac{dA_{kj}}{dT}-\ln\left(A_{jk}A_{kj}\right)\left(\frac{\sum_{p=1}^{N}x_p\frac{dA_{jp}}{dT}}{\sum_{p=1}^{N}x_pA_{jp}}+\frac{\sum_{q=1}^{N}x_q\frac{dA_{kq}}{dT}}{\sum_{q=1}^{N}x_qA_{kq}}\right)\right]}{\sum_{p=1}^{N}x_pA_{jp}+\sum_{q=1}^{N}x_qA_{kq}}$$

$$+RT^2\left(\frac{\sum_{j=1}^{N}x_j\frac{dV_j}{dT}}{\sum_{j=1}^{N}x_jV_j}-\sum_{j=1}^{N}x_j\frac{\frac{dV_j}{dT}}{V_j}\right) \qquad (6.2.1.5)$$

where

$$\frac{dA_{jk}}{dT}=\frac{\beta A_{jk}}{T}\left[1+\frac{2}{\ln\left(A_{jk}A_{kj}\right)-2}\right] \qquad (6.2.1.6)$$

and

$$\frac{dV_j}{dT}=\left(\frac{-2V_j\ln Z_{RAj}}{7T_{cj}}\right)\left(1-\frac{T}{T_{cj}}\right)^{-5/7} \qquad (6.2.1.7)$$

where N is taken as 3 and the value of β is equal to 2.

Table 6.8: Values of the Parameters A_{ij} and A_{ji}, Relative Root Mean Square (RRMS) Errors in Liebermann-Fried Model Calculations for Ethanol(1)+Cyclohexane(3) and *n*-Hexane(2)+Cyclohexane(3) Mixtures at 298.15 K

Component i	Component j	A_{ij}	A_{ji}	RRMS
Ethanol	Cyclohexane	0.5916	1.0346	15.839
n-Hexane	Cyclohexane	0.6748	1.2600	2.757

An attempt is made to apply the Liebermann-Fried model to estimate the $H^E_{m,123}$ values with the values of the Liebermann-Fried interaction parameters A_{ij} and A_{ji} for

the constituent-binary mixtures given in Tables 6.7 and 6.8. However, the Liebermann-Fried model could not satisfactorily estimate the $H^{E}_{m,123}$ values of the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture, and are not presented in this Chapter. The likely reason for this is due to the large errors accumulated from the constituent-binary mixtures in representing the $H^{E}_{m,ij}$ values.

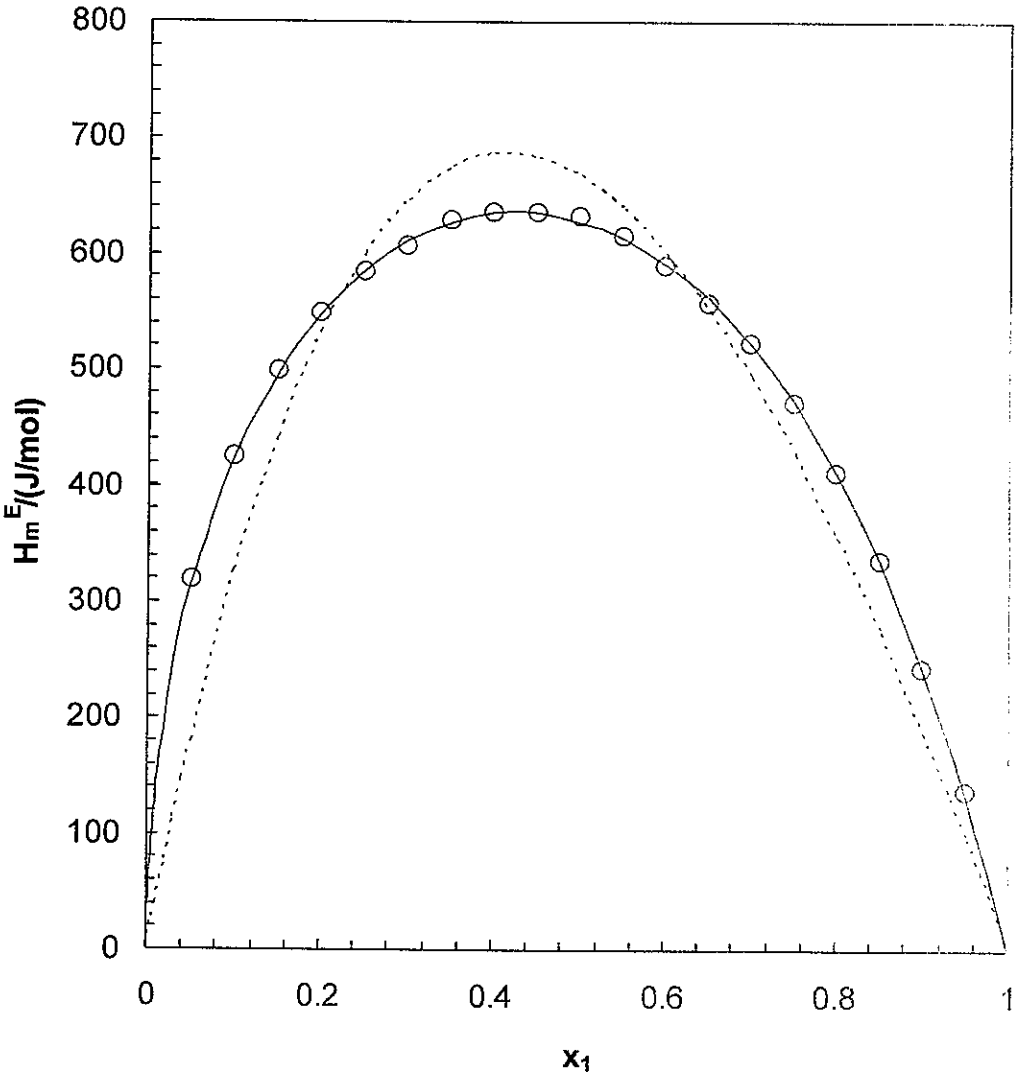

Figure 6.9: Excess Molar Enthalpies for Ethanol(1)+Cyclohexane(3) System at 298.15 K. o, Experimental Results; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from Liebermann-Fried Model Equation (6.2.1.1).

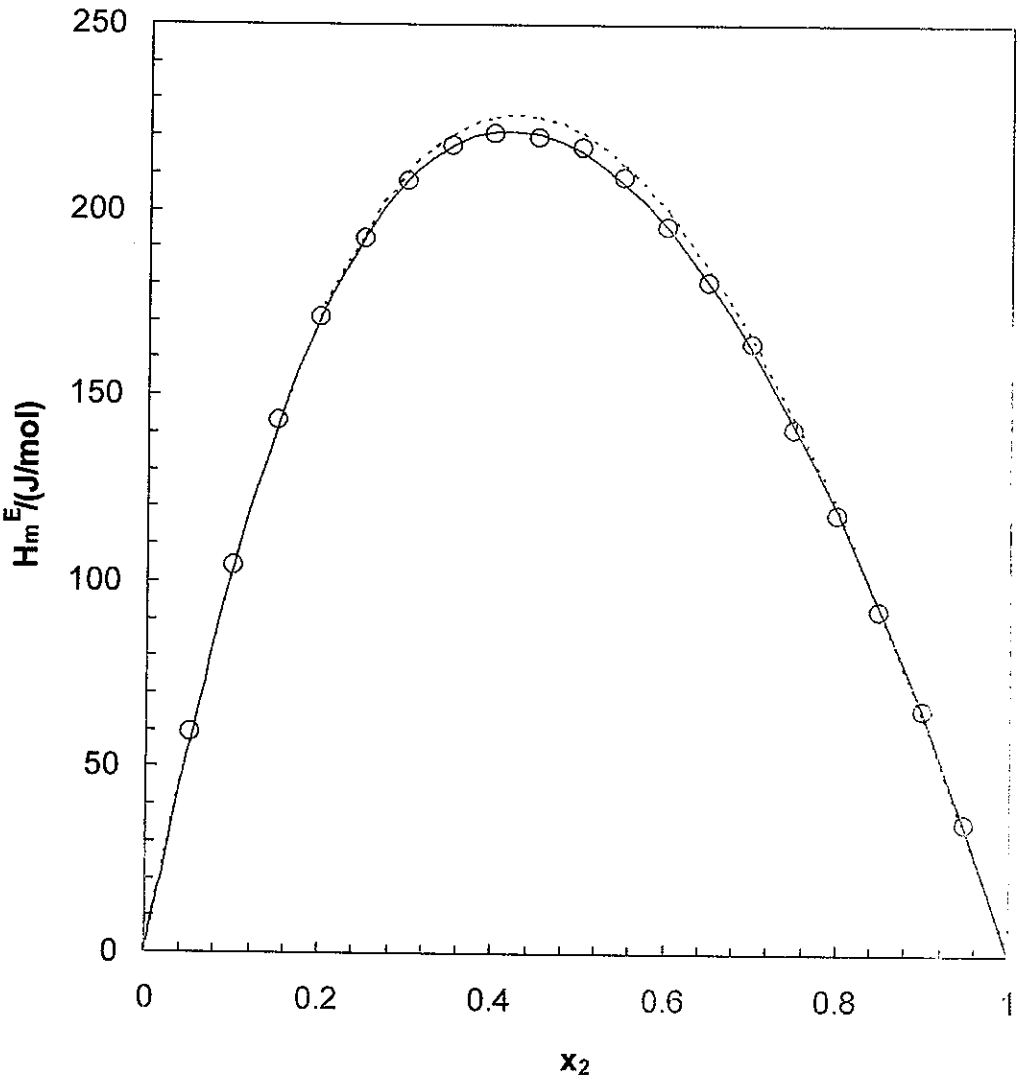

Figure 6.10: Excess Molar Enthalpies for *n*-Hexane(2)+Cyclohexane(3) System at 298.15 K. o, Experimental Results; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from Liebermann-Fried Model Equation (6.2.1.1).

6.2.2 Flory Theory

Previously the Flory theory (Flory, 1965; Abe and Flory, 1965) was used to correlate the excess molar enthalpies of binary mixtures in the work of Wang *et al.* (1993). An attempt is made in this work to represent excess molar enthalpies with the Flory theory. The equations used to represent the excess molar enthalpies of binary

mixtures by the Flory theory are summarized in this Section. The applicable Flory theory in reduced form for pure components and mixtures is given by

$$\frac{\overline{P}\overline{v}}{\overline{T}} = \frac{\overline{v}^{1/3}}{\overline{v}^{1/3}-1} - \frac{1}{\overline{v}\overline{T}} \qquad (6.2.2.1)$$

which can be reduced to

$$\overline{v}^{4/3}\overline{T} - \overline{v}^{1/3} + 1 = 0 \qquad (6.2.2.2)$$

at zero pressure.

The reduced quantities are defined in the following equations:

$$\overline{v} = \frac{v}{v^*} \qquad (6.2.2.3)$$

$$\overline{T} = \frac{T}{T^*} \qquad (6.2.2.4)$$

$$\overline{P} = \frac{P}{P^*} \qquad (6.2.2.5)$$

The asterisk refers to the characteristic values of the pressure, P, volume, V, and temperature T. The values v_i^* and P_i^* for pure components can be obtained from

$$\overline{v}_i^{1/3} = \left(\frac{v_{m,i}}{v_i^*}\right)^{1/3} = 1 + \frac{\alpha_{p,i}T}{3\left(1+\alpha_{p,i}T\right)} \qquad (6.2.2.6)$$

and

$$P_i^* = \left(\frac{\alpha_{p,i}}{\kappa_{T,i}}\right)T\overline{v}_i^2 \qquad (6.2.2.7)$$

where $v_{m,i}$, $\alpha_{p,i}$ and $\kappa_{T,i}$ stand for the molar volume, isobaric expansivity and isothermal compressibility, respectively. The corresponding values of these properties for pure substances that comprise the ternary mixture studied in this work are listed in Table 6.9. The values of T_i^* can be calculated from Equations (6.2.2.2) and (6.2.2.4).

The segment fractions, ϕ_j, and the site fractions, θ_j, are defined in the following equations, respectively:

$$\phi_j = \frac{x_j v_j^*}{\sum x_i v_i^*} \qquad (6.2.2.8)$$

$$\theta_j = \frac{\phi_j}{\sum \phi_i (s_i / s_j)} \tag{6.2.2.9}$$

where s_i is the number of contact sites per segment of a molecule of species *i*. As the molecules are approximately spherical (Wang *et al.*, 1993), one has

$$\frac{s_i}{s_j} = \left(\frac{v_j^*}{v_i^*}\right)^{1/3} \tag{6.2.2.10}$$

Table 6.9: Parameters Used in Flory Theory at 298.15 K

Substance	$v_{m,i}$ /cm^3·mol^{-1}	$\alpha_{p,i}$ /k·K^{-1}	$\kappa_{T,i}$ /T·Pa^{-1}
Ethanol	58.68	1.083	1167
n-Hexane	131.59	1.387	1703.9
Cyclohexane	108.83	1.220	1140

The expression for excess molar enthalpy is represented in the form:

$$H_m^E = \left(\sum x_i v_i^*\right) \sum \left\{ \phi_i P_i^* \left(\tilde{v}_i^{-1} - \tilde{v}^{-1}\right) + \tilde{v}^{-1} \psi \right\} \tag{6.2.2.11}$$

where

$$\tilde{v} = \sum \phi_i \tilde{v}_i \tag{6.2.2.12}$$

for binary mixtures,

$$\psi = \phi_1 \theta_2 X_{12} \tag{6.2.2.13}$$

and for ternary mixtures,

$$\psi = \phi_1 \theta_2 X_{12} + \phi_2 \theta_3 X_{23} + \phi_3 \theta_1 X_{13} s_3 / s_1 \tag{6.2.2.14}$$

The interchange interaction energy parameters, X_{ij} in Equations (6.2.2.13) and (6.2.2.14) are determined from a least-squares method in which Equations (6.2.2.11) is fitted to the experimental data of $H_{m,ij}^E$ for the constituent-binary mixtures of the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture. Another parameter, X_{ji} is obtained via the following relation:

$$X_{ij} = X_{ji} \left[\frac{v_{m,j}^*}{v_{m,i}^*}\right]^{1/3} \tag{6.2.2.15}$$

Table 6.10 lists the values of parameters X_{ij} and X_{ji} determined in this work.

Figures 6.11 - 6.13 illustrate the comparisons of the calculated values obtained from the Flory theory and the regression expression, Equation (6.1.3.1.1), with the experimental data for the ethanol(1)+*n*-hexane(2), ethanol(1)+cyclohexane(3) and *n*-hexane(2)+cyclohexane(3) mixtures. It can be seen that the Flory theory tends to yield curves that shift a little to the right hand in comparison with the calculated values obtained from the regression expression for the three constituent-binary mixtures. The accumulated deviations from the constituent-binary mixtures lead to unsatisfactory excess molar enthalpies for the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture and are not discussed further in this Chapter.

Table 6.10: Values of the Parameters X_{ij} and X_{ji} in Flory Theory Calculations for Constituent-binary Mixtures of Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) Mixture at 298.15 K

Component i	Component j	X_{ij}/J·cm^{-3}	X_{ji}/J·cm^{-3}
Ethanol	*n*-Hexane	44.66	34.63
Ethanol	Cyclohexane	57.01	46.73
n-Hexane	Cyclohexane	9.79	10.35

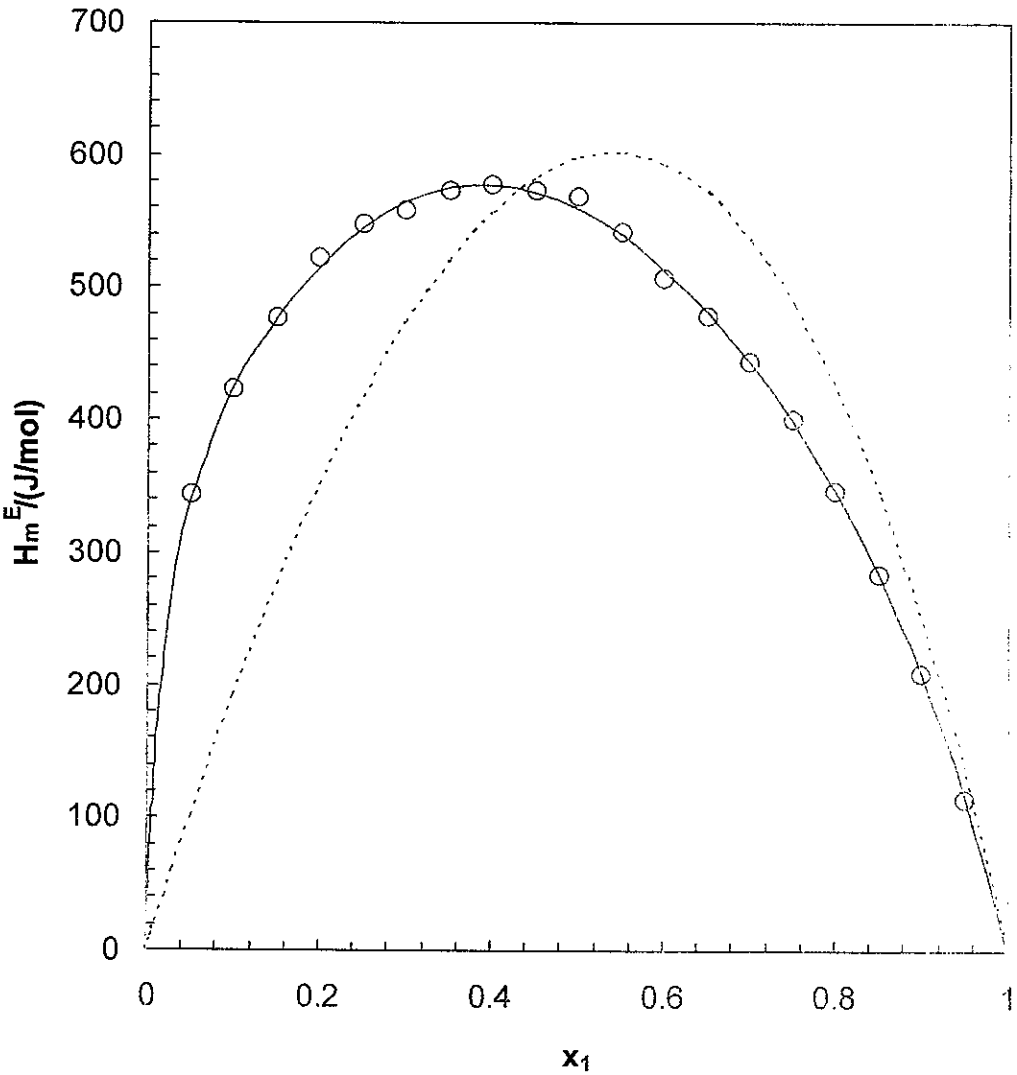

Figure 6.11: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at 298.15 K. o, Experimental Results; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from the Flory Theory Equation (6.2.2.11).

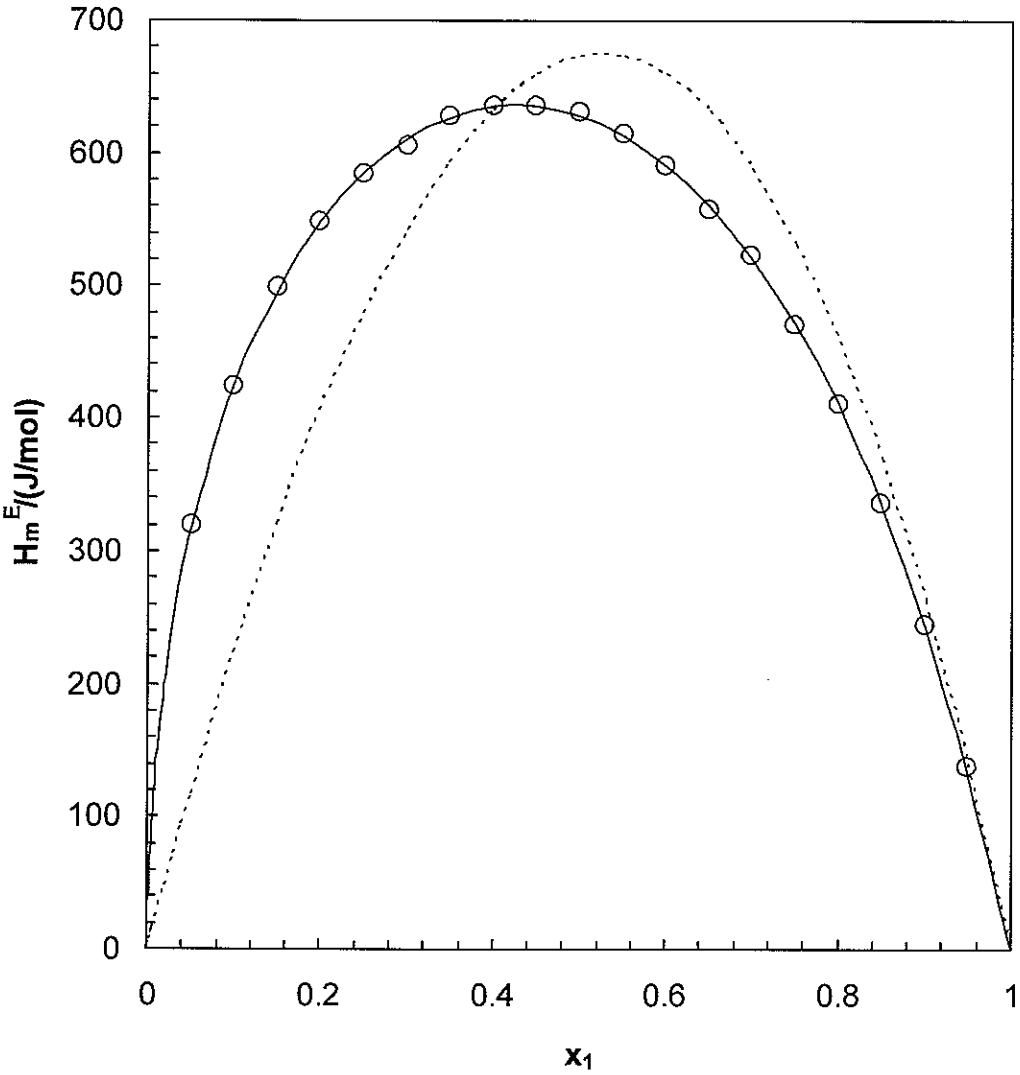

Figure 6.12: Excess Molar Enthalpies for Ethanol(1)+Cyclohexane(3) System at 298.15 K. o, Experimental Results; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from the Flory Theory Equation (6.2.2.11).

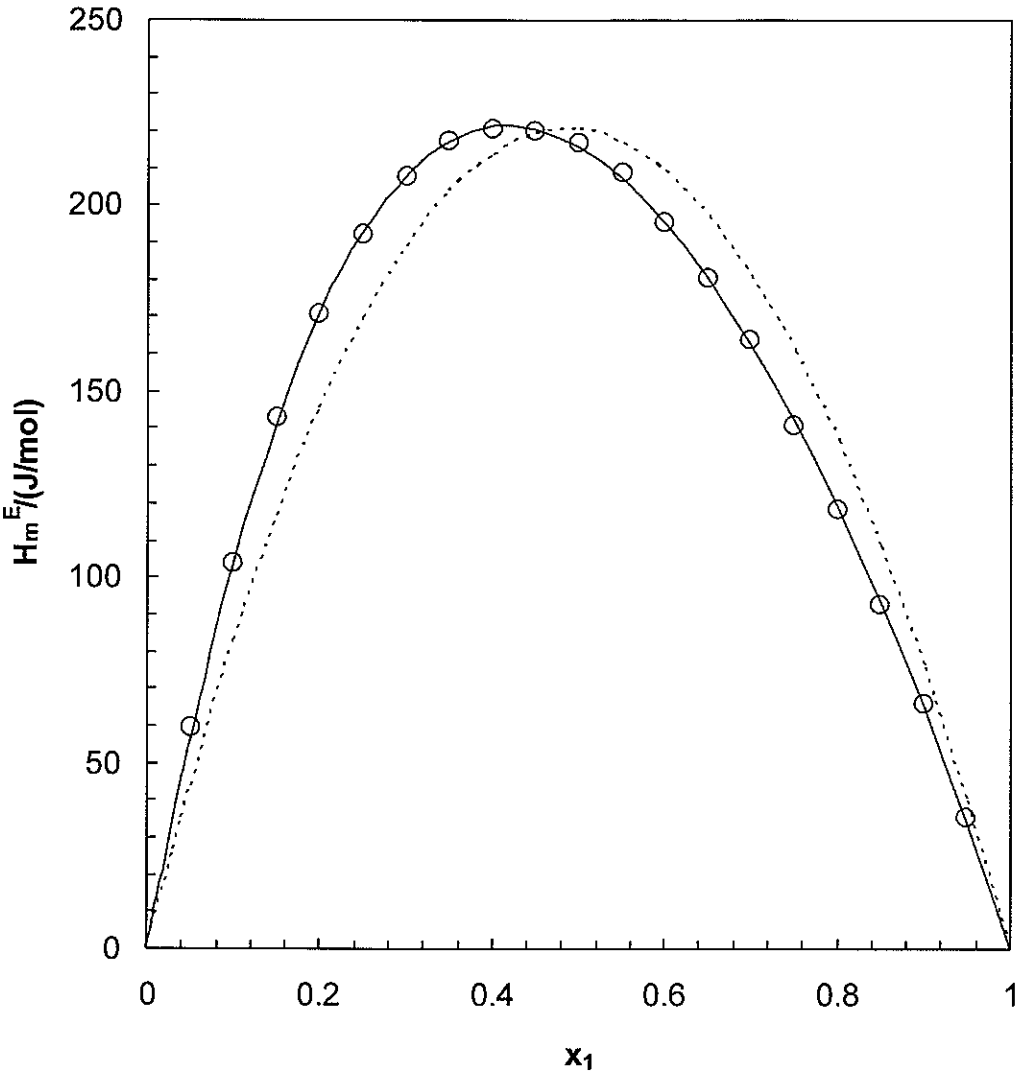

Figure 6.13: Excess Molar Enthalpies for *n*-Hexane(2)+Cyclohexane(3) System at 298.15 K. o, Experimental Results; —, Calculated from the Regression Equation (6.1.3.1.1); ----, Calculated from the Flory Theory Equation (6.2.2.11).

CHAPTER 7
EXCESS ENTHALPY CALCULATIONS

7.1 Application of the PPR-3 Model to the Excess Enthalpy Calculations

The excess molar enthalpy data of the ethanol+*n*-hexane+cyclohexane ternary mixture and its constituent-binary mixtures were measured in this work. The Model PPR-3, which has been shown in Chapter 5 to represent well the phase behavior of alkanol with hydrocarbon mixtures, is used here to estimate the excess enthalpy values of binary and multicomponent systems involving only one associating component.

The excess molar enthalpy of binary and multicomponent systems is defined as

$$H^E = (H - H^*)_{mixture} - \sum_{i=1}^{n} x_i (H_i - H_i^*)_{pure} \qquad (7.1.1)$$

where n has the value of two for a binary mixture and is greater than two for multicomponent systems. $(H_i - H_i^*)_{pure}$ and $(H - H^*)_{mixture}$ are the enthalpy departure functions of pure compounds and mixtures, respectively, and can be calculated from the following expression:

$$(H - H^*)_{\text{pure or mixture}} = Pv - RT + \int_{\infty}^{v} \left[P - T\left(\frac{\partial P}{\partial T}\right)_v \right] dv \qquad (7.1.2)$$

In Equation (7.1.2), the partial derivative of the pressure, P, with respect to temperature, T, must be evaluated. A suitable equation of state is chosen to serve this purpose. If the original PR EOS is adopted to describe a pure non-associating compound, then the derivative of the pressure with respective to the temperature in Equation (7.1.2) is given by

$$\left(\frac{\partial P}{\partial T}\right)_{v,\text{na}} = \frac{R}{v_{\text{na}} - b_{\text{na}}} - \frac{\partial a_{\text{na}} / \partial T}{v_{\text{na}}^2 + 2b_{\text{na}} v_{\text{na}} - b_{\text{na}}^2} \qquad (7.1.3)$$

Upon substituting Equation (7.1.3) into Equation (7.1.2), one obtains the following expression for the enthalpy departure function of a pure non-associating compound:

$$\left(H-H^*\right)_{\text{nonassociating}} = Pv_{na} - RT + \frac{(\partial a_{na}/\partial T)T - a_{na}}{2\sqrt{2}b_{na}} \ln \frac{v_{na}+(1+\sqrt{2})b_{na}}{v_{na}+(1-\sqrt{2})b_{na}} \qquad (7.1.4)$$

For an associating compound, the required partial derivative of Model PPR-3 is

$$\left(\frac{\partial P}{\partial T}\right)_{v,a} = \left[\frac{\partial(n_T/n_0)}{\partial T}\right]\frac{RT}{v_a-b_a} + \frac{n_T}{n_0}\left[\frac{R}{v_a-b_a} + \frac{RT(\partial b_a/\partial T)}{(v_a-b_a)^2}\right]$$

$$-\frac{\partial a_a/\partial T}{v_a^2+2b_av_a-b_a^2} + \frac{2a_a(v_a-b_a)(\partial b_a/\partial T)}{(v_a^2+2b_av_a-b_a^2)^2} \qquad (7.1.5)$$

The enthalpy departure function of an associating compound can then be written as

$$\left(H-H^*\right)_{\text{associating}} = Pv_a - RT + \frac{(\partial a_a/\partial T)T - a_a}{2\sqrt{2}b_a} \ln \frac{v_a+(1+\sqrt{2})b_a}{v_a+(1-\sqrt{2})b_a}$$

$$+\left(\frac{2}{\left[1+\sqrt{1+4K_aRT/(v_a-b_a)}\right]}-1\right)R(E_{1a}-T) + \frac{T(\partial b_a/\partial T)}{2K_a}\left\{1-\sqrt{1+\frac{4K_aRT}{(v_a-b_a)}}\right\}$$

$$+\frac{a_aT(\partial b_a/\partial T)}{b_a}\left[\frac{v_a}{(v_a^2+2b_av_a-b_a^2)} + \frac{1}{2\sqrt{2}b_a}\ln\frac{v_a+(1-\sqrt{2})b_a}{v_a+(1+\sqrt{2})b_a}\right] \qquad (7.1.6)$$

where the expressions of the temperature-dependent parameters a_{na} and b_{na} for a non-associating compound, and a_a, b_a and E_{1a} for a pure associating compound using Model PPR-3 have been given in Chapter 4.

For the binary mixtures in which component 1 is an associating species, such as an alkanol, and component 2 is a non-associating species, such as a hydrocarbon, the enthalpy departure function is given by

$$(H-H^*)_{mixture} = Pv_{mixture} - RT + \frac{(\partial\bar{a}/\partial T)T - \bar{a}}{2\sqrt{2}\bar{b}} \ln \frac{v_{mixture}+(1+\sqrt{2})\bar{b}}{v_{mixture}+(1-\sqrt{2})\bar{b}}$$

$$+\left(\frac{2}{1+\sqrt{1+4K_1RTx_1/(v_{mixture}-\bar{b})}}-1\right)Rx_1(E_{1a}-T)$$

$$+\frac{T(\partial\bar{b}/\partial T)}{2K_1}\left[1-\sqrt{1+\frac{4K_1RTx_1}{(v_{mixture}-\bar{b})}}\right] - \frac{x_2RT^2(\partial\bar{b}/\partial T)}{(v_{mixture}-\bar{b})}$$

$$+\frac{\bar{a}T(\partial\bar{b}/\partial T)}{\bar{b}}\left[\frac{v_{mixture}}{(v_{mixture}^2+2\bar{b}v_{mixture}-\bar{b}^2)}+\frac{1}{2\sqrt{2}\bar{b}}\ln\frac{v_{mixture}+(1-\sqrt{2})\bar{b}}{v_{mixture}+(1+\sqrt{2})\bar{b}}\right] \quad (7.1.7)$$

where $v_{mixture}$ is the molar volume of the mixture and the mixture parameters $\bar{a}$ and $\bar{b}$ are defined by Equations (3.1.2) and (3.1.3), respectively.

Upon substituting Equations (7.1.4) and (7.1.6) into Equation (7.1.1), one obtains the final expression of excess molar enthalpy of binary mixtures. Following a procedure similar to that is used for binary mixtures; one obtains the expression for excess molar enthalpy of multicomponent systems involving only one associating component. The enthalpy departure function of such systems in which component 1 is the associating species has the form

$$(H-H^*)_{mixture}=Pv_{mixture}-RT+\frac{(\partial\bar{a}/\partial T)T-\bar{a}}{2\sqrt{2}\bar{b}}\ln\frac{v_{mixture}+(1+\sqrt{2})\bar{b}}{v_{mixture}+(1-\sqrt{2})\bar{b}}$$

$$+\left(\frac{2}{\left[1+\sqrt{1+4K_1RTx_1/(v_{mixture}-\bar{b})}\right]}-1\right)Rx_1(E_{1a}-T)$$

$$+\frac{T(\partial\bar{b}/\partial T)}{2K_1}\left[1-\sqrt{1+\frac{4K_1RTx_1}{(v_{mixture}-\bar{b})}}\right]-\frac{\sum_{j=2}^{n}x_jRT^2(\partial\bar{b}/\partial T)}{(v_{mixture}-\bar{b})}$$

$$+\frac{\bar{a}T(\partial\bar{b}/\partial T)}{\bar{b}}\left[\frac{v_{mixture}}{(v_{mixture}^2+2\bar{b}v_{mixture}-\bar{b}^2)}+\frac{1}{2\sqrt{2}\bar{b}}\ln\frac{v_{mixture}+(1-\sqrt{2})\bar{b}}{v_{mixture}+(1+\sqrt{2})\bar{b}}\right] \quad (7.1.8)$$

The excess molar enthalpy of a multicomponent system can be calculated from the following equation:

$$H^E=(H-H^*)_{mixture}-x_1(H_1-H_1^*)_{associating}-\sum_{i=2}^{n}x_i(H_i-H_i^*)_{nonassociating} \quad (7.1.9)$$

7.2 Application of the Wilson Equation to the Excess Enthalpy Calculations

The general form of the Wilson equation is written as

$$\frac{G^E}{RT} = -\sum_i x_i \ln \sum_j x_j \Lambda_{ij} \tag{7.2.1}$$

The parameter Λ_{ij} is related to the molar volumes, v_i^L and v_j^L, of the pure compounds and to the characteristic energy differences A_{ij} by the relations:

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) = \frac{v_j^L}{v_i^L} \exp\left(-\frac{A_{ij}}{RT}\right) \tag{7.2.2}$$

For a binary system, Equation (7.2.1) reduces to the form:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(\Lambda_{21} x_1 + x_2) \tag{7.2.3}$$

The expression for calculating the excess molar enthalpy is obtained by applying the relation:

$$H^E = -RT^2 \frac{\partial(\frac{G^E}{RT})}{\partial T} \tag{7.2.4}$$

Thus, the working equation for calculating the excess molar enthalpy of a multicomponent system has the form:

$$H^E = RT^2 \sum_i \frac{x_i \left(\sum_j x_j \frac{d\Lambda_{ij}}{dT}\right)}{\sum_j x_j \Lambda_{ij}} \tag{7.2.5}$$

For a binary system, the above equation reduces to the form:

$$H^E = x_1 x_2 RT^2 \left(\frac{\frac{d\Lambda_{12}}{dT}}{x_1 + \Lambda_{12} x_2} + \frac{\frac{d\Lambda_{21}}{dT}}{\Lambda_{21} x_1 + x_2} \right) \tag{7.2.6}$$

As the Λ_{12} and Λ_{21} values for the ethanol(1)+*n*-hexane(2) system as presented by Wolff and Gotz (1976) in Table 7.1 are temperature-dependent, two cases will be considered as follows:

- Case 1: The parameter values Λ_{12} and Λ_{21} for the ethanol(1)+*n*-hexane(2) system can be correlated with temperature by the following quadratic functions:

$$\Lambda_{12} = a_2 (T/\mathrm{K})^2 + a_1 (T/\mathrm{K}) + a_0 \tag{7.2.7}$$

$$\Lambda_{21} = b_2 (T/\mathrm{K})^2 + b_1 (T/\mathrm{K}) + b_0 \qquad (7.2.8)$$

where

$a_2 = 1.787321\times10^{-5}$, $a_1 = -9.983848\times10^{-3}$, $a_0 = 1.434439$

$b_2 = -1.069286\times10^{-5}$, $b_1 = 7.954351\times10^{-3}$, $b_0 = -1.190969$

then the excess molar enthalpy values of the ethanol(1)+*n*-hexane(2) system can be evaluated from the Equation (7.2.6).

- Case 2: The characteristic energies A_{ij} are often assumed independent of temperature. Equation (7.2.6) can then be simplified to

$$H^E = x_1 x_2 \left(\frac{\Lambda_{12} A_{12}}{x_1 + \Lambda_{12} x_2} + \frac{\Lambda_{21} A_{21}}{x_2 + \Lambda_{21} x_1} \right) \qquad (7.2.9)$$

The Wilson parameters Λ_{13} and Λ_{31} for the ethanol(1)+cyclohexane(3) system were correlated by Scatchard and Satkiewicz (1964) in the following forms:

$$\Lambda_{13} = c_2/(T/\mathrm{K})^2 + c_1/(T/\mathrm{K}) + c_0 \qquad (7.2.10)$$

$$\Lambda_{31} = d_1/(T/\mathrm{K}) + d_0 \qquad (7.2.11)$$

where

$c_2 = 67100$, $c_1 = -532$, $c_0 = 1.0757$

$d_1 = -120.71$, $d_0 = 0.658$

Therefore, case 1 and case 2 will be considered in the excess molar enthalpy calculations of the ethanol(1)+cyclohexane(3) system.

For a multicomponent system, i.e. ethanol(1)+*n*-hexane(2)+cyclohexane(3) ternary system, Equation (7.2.5) can be used in the excess molar enthalpy calculations by means of the Wilson equation with temperature-dependent parameters Λ_{12} and Λ_{21} in Equations (7.2.7 - 7.2.8) and Λ_{13} and Λ_{31} in Equations (7.2.10 – 7.2.11). The parameters A_{23} and A_{32} in Table 7.1 are assumed to be constant for the *n*-hexane(2)+cyclohexane(3) system because the relationship of the Wilson parameters and the temperature is not available for this system. Therefore the parameters Λ_{23} and Λ_{32} can be calculated from Equation (7.2.2). If the Wilson equation with temperature-independent parameters A_{ij} and A_{ji} is applied in the excess molar enthalpy calculation, then Equation (7.2.5) is reduced to the following form:

$$H^E = \sum_i \frac{x_i \left(\sum_j x_j \Lambda_{ij} A_{ij} \right)}{\sum_j x_j \Lambda_{ij}} \qquad (7.2.12)$$

Table 7.1: Parameter Values in the Wilson Equation

T/K	Component		Λ_{ij}	Λ_{ji}	A_{ij}	A_{ji}	VLE Data Source
	i	j	cal·mol^{-1}		cal·mol^{-1}		
298.15	Ethanol	*n*-Hexane			2133.6913	395.0508	Smith and Robinson (1970)
303.15	Ethanol	*n*-Hexane	0.04986	0.23663	2293	381	Wolff and Gotz (1976)
313.15	Ethanol	*n*-Hexane	0.06128	0.25269	2242	351	Wolff and Gotz (1976)
323.15	Ethanol	*n*-Hexane	0.07525	0.26443	2184	331	Wolff and Gotz (1976)
333.15	Ethanol	*n*-Hexane	0.09178	0.27049	2123	324	Wolff and Gotz (1976)
343.15	Ethanol	*n*-Hexane	0.11191	0.27841	2053	312	Wolff and Gotz (1976)
353.15	Ethanol	*n*-Hexane	0.13842	0.28555	1967	300	Wolff and Gotz (1976)
298.15	*n*-Hexane	Cyclohexane			268.2948	-115.4906	Martin and Youings (1980)

7.3 Results and Discussion

An attempt is made to simultaneously represent VLE and excess enthalpy behavior of the binary and ternary mixtures in which only one component is an associating species by means of Model PPR-3 and the Wilson equation.

Model PPR-3 is applied to the excess molar enthalpy predictions of the ethanol(1)+*n*-hexane(2) mixture with the binary interaction parameter, δ_{12}, and the ethanol(1)+cyclohexane(3) mixture with δ_{13}, and the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixtures with three binary interaction parameters, δ_{12}, δ_{13} and δ_{23}. The values of coefficients in the δ_{12} and δ_{13} expressions have been given in Chapter 5. The value of the binary interaction parameter, δ_{23} for the *n*-hexane(2)+cyclohexane(3) mixture at 298.15 K is set equal to zero. The programs for the excess molar enthalpy calculations of associating mixtures are attached in Appendix B.

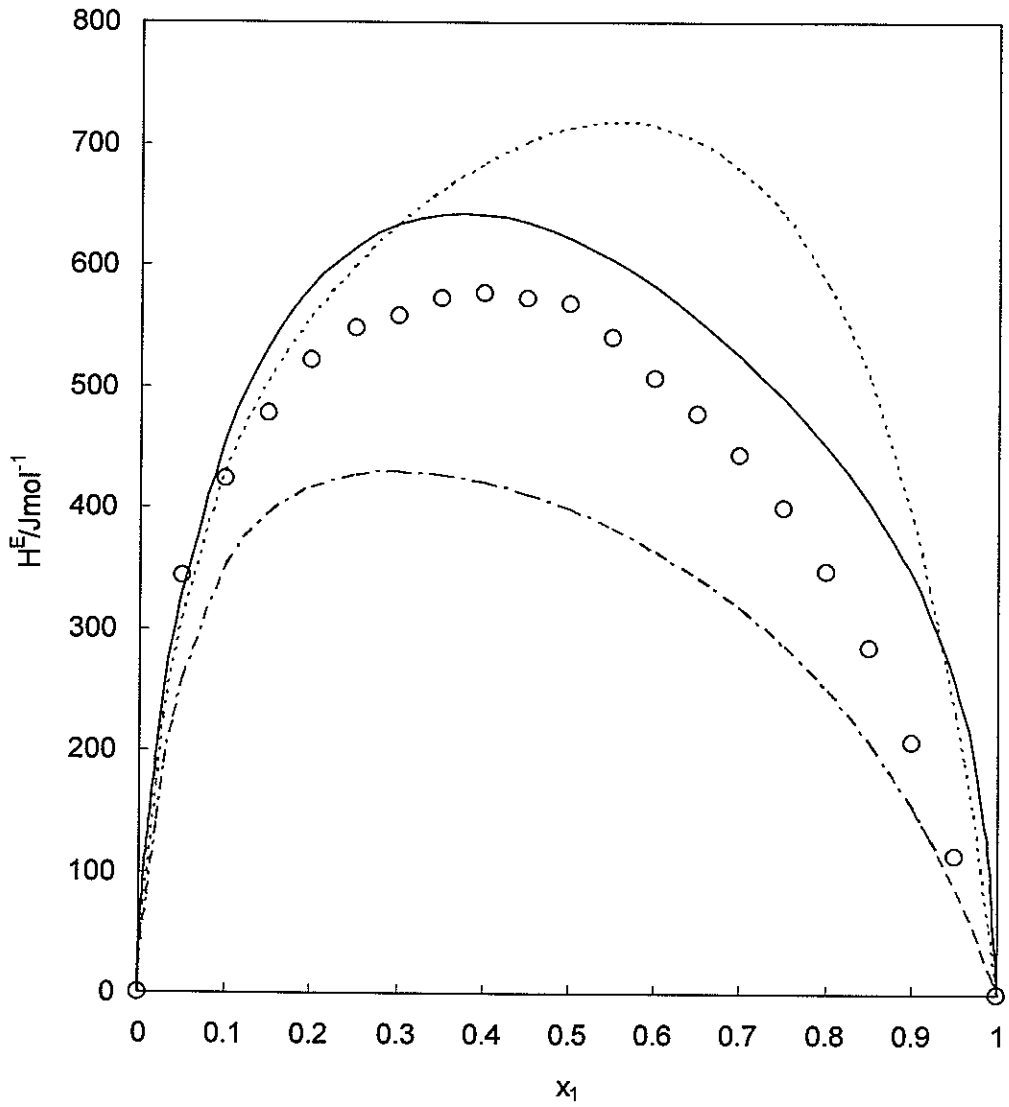

Figure 7.1: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at 298.15 K. o, Experimental Results; —, Calculated from Model PPR-3 (δ_{12}=-0.0251); ----, Calculated from the Wilson Equation with Temperature-dependent Parameters Λ_{12} and Λ_{21} in Equations (7.2.7 - 7.2.8); – – – –, Calculated from the Wilson Equation with Temperature-independent Parameters A_{12} and A_{21} in Table 7.1.

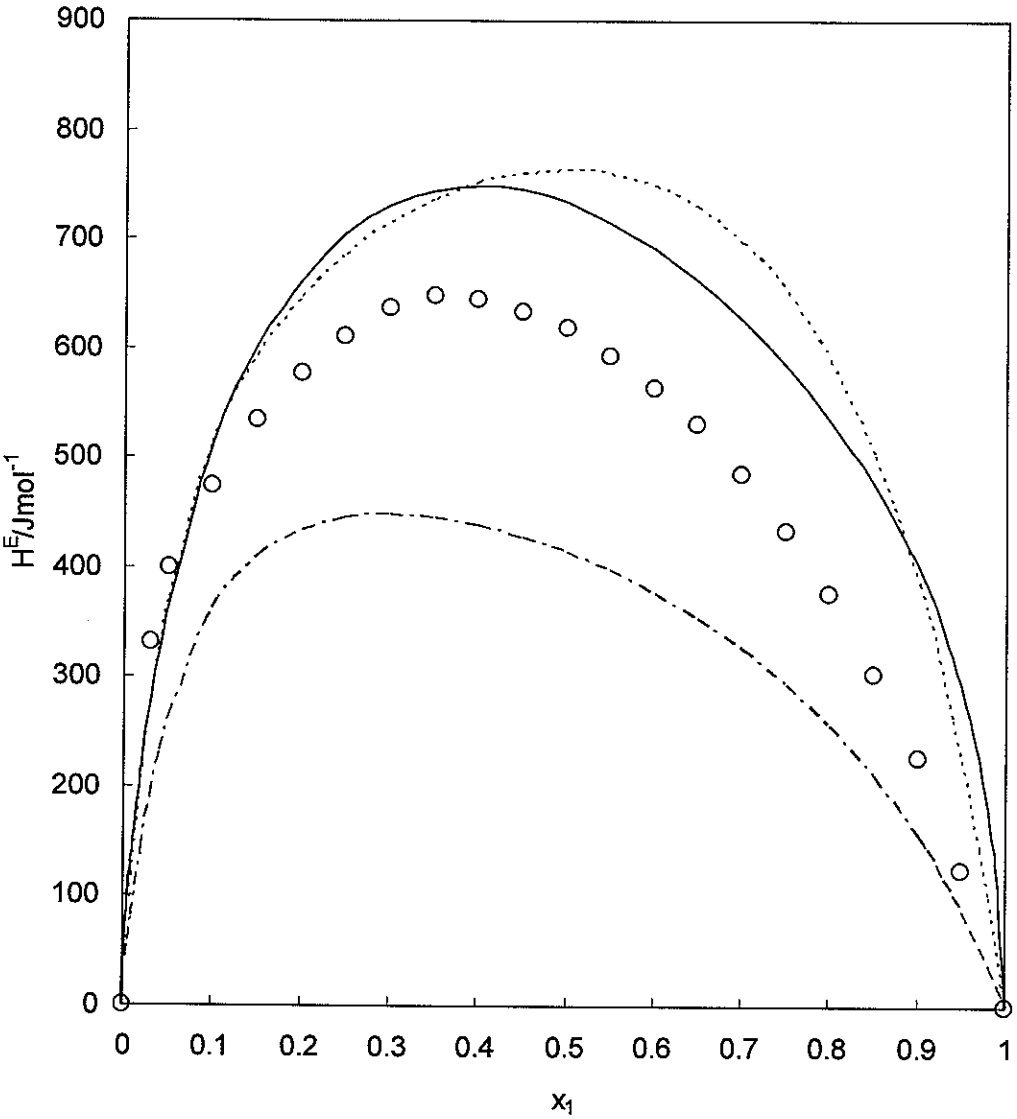

Figure 7.2: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at 303.15 K. o, Experimental Results; —, Calculated from Model PPR-3 (δ_{12} =-0.0219); ----, Calculated from the Wilson Equation with Temperature-dependent Parameters Λ_{12} and Λ_{21} in Equations (7.2.7 – 7.2.8); ----, Calculated from the Wilson Equation with Temperature-independent Parameters A_{12} and A_{21} in Table 7.1.

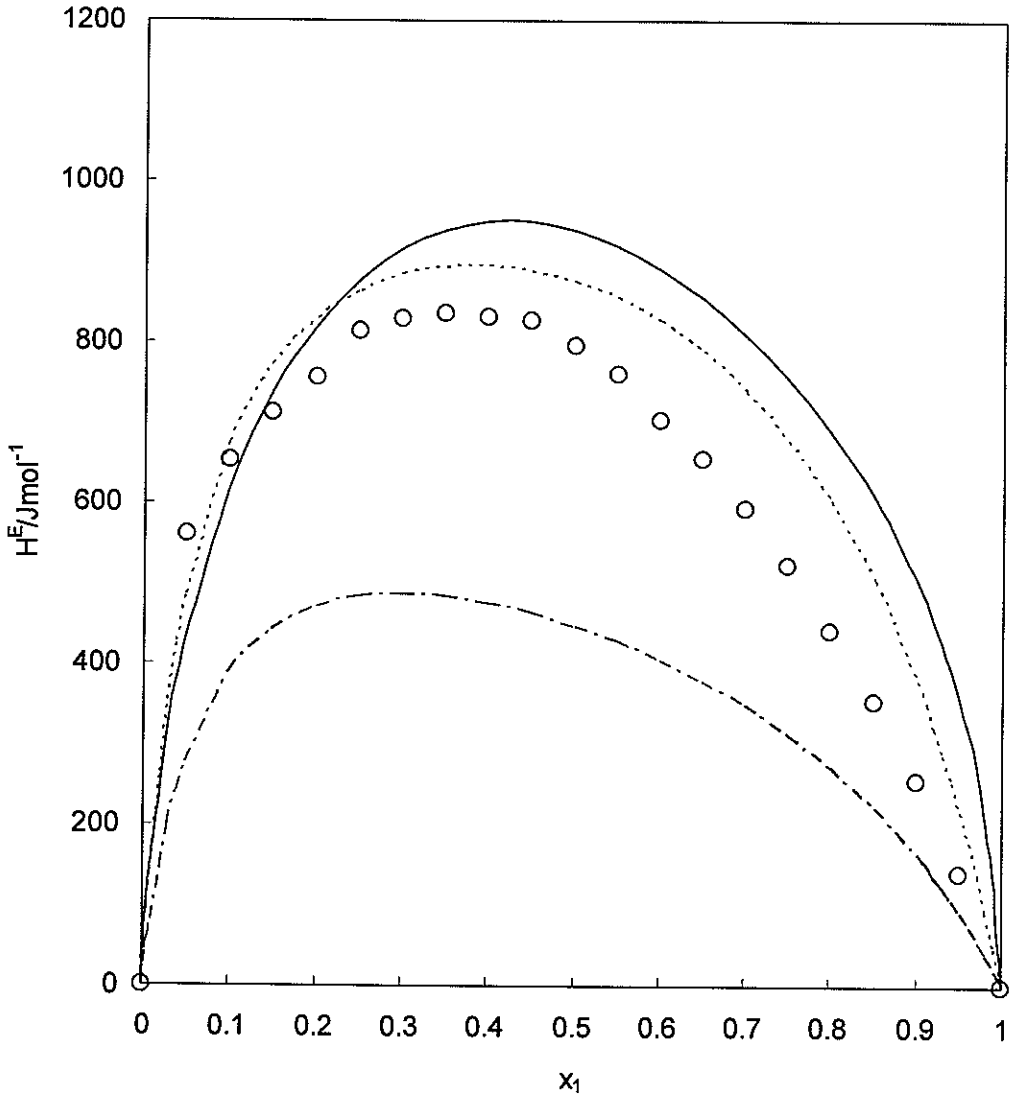

Figure 7.3: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2) System at 313.15 K. o, Experimental Results; —, Calculated from Model PPR-3 (δ_{12}=-0.0184); ----, Calculated from the Wilson Equation with Temperature-dependent Parameters Λ_{12} and Λ_{21} in Equations (7.2.7 – 7.2.8); – – – –, Calculated from the Wilson Equation with Temperature-independent Parameters A_{12} and A_{21} in Table 7.1.

Figures 7.1 illustrates the predicted excess molar enthalpy values of the ethanol(1)+*n*-hexane(2) mixture at 298.15 K using Model PPR-3 and the Wilson equation with temperature-dependent and temperature-independent parameters, respectively. It can be clearly seen that the results calculated by means of Model PPR-3

with one binary interaction parameter appear to be more accurate than the values generated by the Wilson equation with two temperature-dependent parameters Λ_{12} and Λ_{21}, and with two temperature-independent parameters A_{12} and A_{21}, in comparison with the experimental data. It should be mentioned that the predicted excess molar enthalpy values from the Wilson equation with temperature-dependent parameters Λ_{12} and Λ_{21}, yield curves which are skewed towards high ethanol mole fraction. This tendency is contrary to the experimental data curve and the predicted results obtained from Model PPR-3.

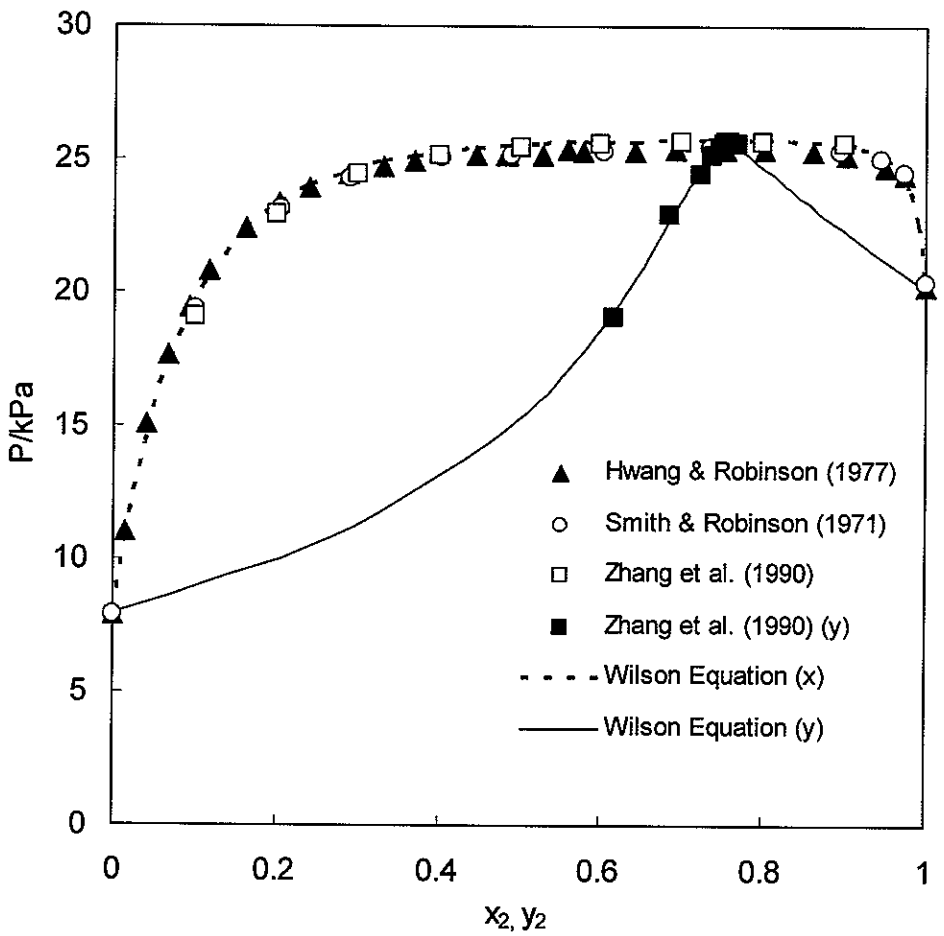

Figure 7.4: VLE for Ethanol(1)+*n*-Hexane(2) System at 25°C

Figures 7.2 and 7.3 show the predicted excess molar enthalpy values of the ethanol(1)+*n*-hexane(2) mixture at 303.15 K and 313.15 K by applying Model PPR-3

and the Wilson equation, respectively. It is evident that Model PPR-3 gives an improvement over the Wilson equation with temperature-dependent and temperature-independent parameters in predicting the excess molar enthalpy of this ternary system at 303.15 K. However, the predicted results from Model PPR-3 are not as good as those by means of the Wilson equation with temperature-dependent parameters Λ_{12} and Λ_{21} whereas they are much better than the results from the Wilson equation with temperature-independent parameters at 313.15 K. As expected, the Wilson equation with temperature-dependent parameters gives a better fit of the experimental data as compared with the Wilson equation with temperature-independent parameters.

Figure 7.4 illustrates the comparison of the calculated VLE results from the Wilson equation with the extrapolated parameter values calculated with the correlating Equations (7.2.7 – 7.2.8), with the experimental data (Hwang and Robinson, 1977; Smith and Robinson, 1971; Zhang *et al.*, 1990). It can be seen that the VLE values calculated from the Wilson equation are fitted with the experimental data very well. This example shows the capability of the Wilson equation in representing both VLE and excess enthalpy behavior with reasonable accuracy.

The comparison of predicted excess molar enthalpies of the ethanol(1)+cyclohexane(3) mixture at 298.15 K calculated by means of Model PPR-3 and the Wilson equation is illustrated in Figure 7.5. The comparison serves to show that Model PPR-3 is better than the Wilson equation with temperature-independent parameters and worse than the Wilson equation with temperature-dependent parameters in predicting the excess molar enthalpies of the ethanol(1)+cyclohexane(3) mixture.

The VLE results calculated from the Wilson equation with the parameter values calculated with the correlating Equations (7.2.10 – 7.2.11) are presented in Figure 7.6. The fact that the calculated values are in good agreement with the experimental data (Hwang and Robinson, 1977; Washburn and Handorf, 1935), indicates that the Wilson equation is capable of predicting the VLE and excess enthalpy behavior simultaneously with the same parameters.

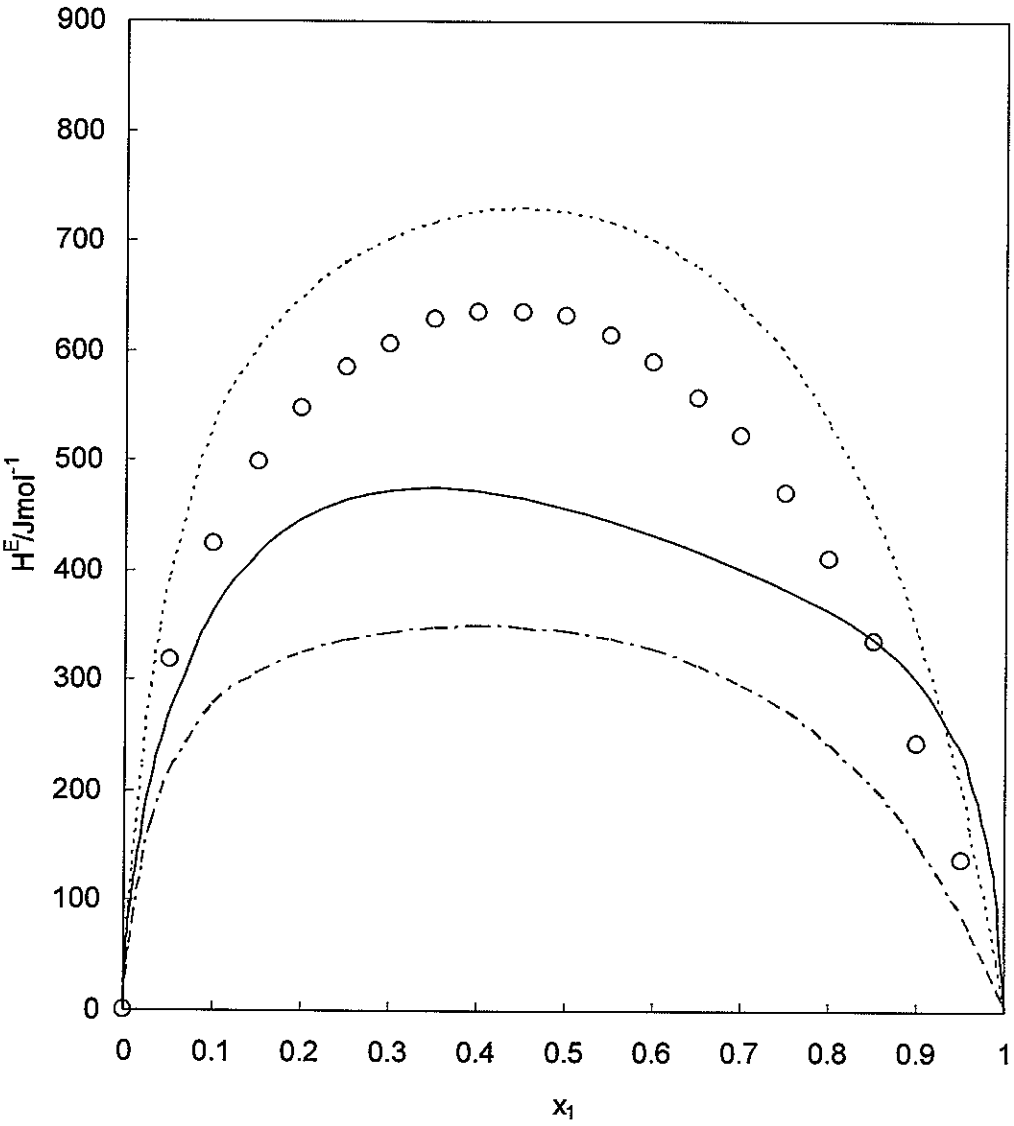

Figure 7.5: Excess Molar Enthalpies for Ethanol(1)+Cyclohexane(3) System at 298.15 K. o, Experimental Results; —, Calculated from Model PPR-3 (δ_{13}=-0.0277); ----, Calculated from the Wilson Equation with Temperature-dependent Parameters Λ_{13} and Λ_{31} in Equations (7.2.10 - 7.2.11); – – – –, Calculated from the Wilson Equation with Temperature-independent Parameters A_{13} and A_{31} in Table 7.1.

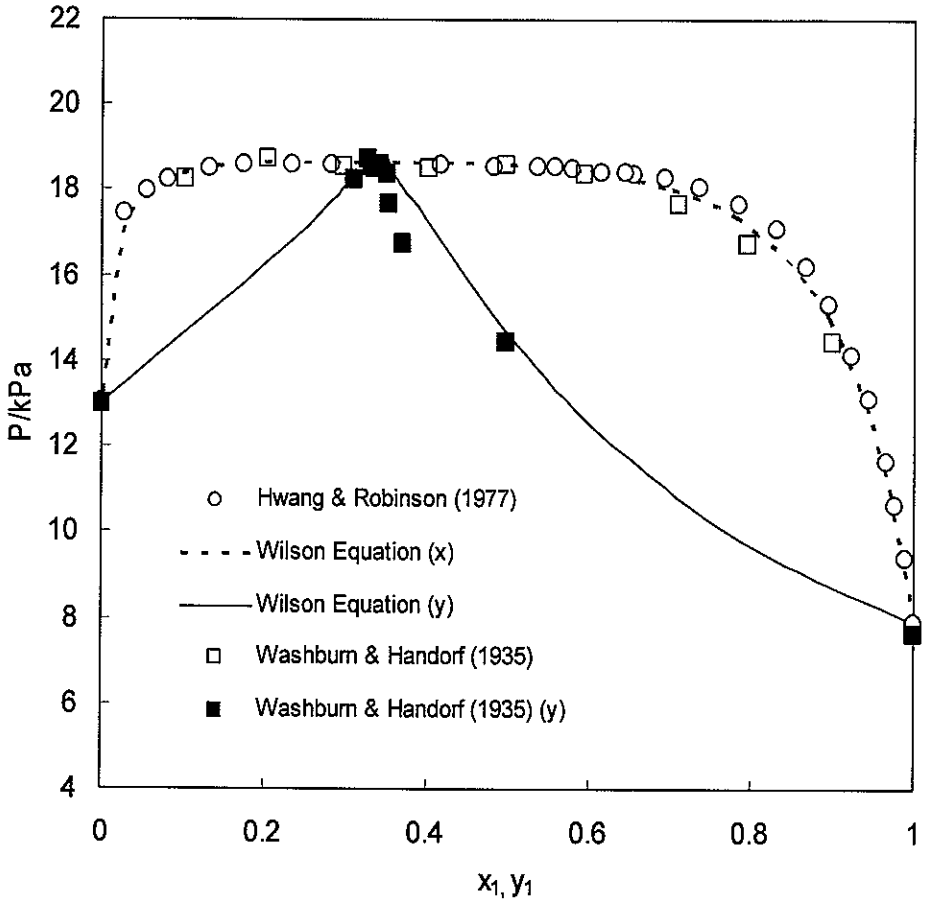

Figure 7.6: VLE for Ethanol(1)+Cyclohexane(3) System at 25°C

Both Model PPR-3 and the Wilson equation can be extended to predict excess molar enthalpies of the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture at 298.15 K with binary interaction parameters correlated from the experimental VLE data of the three constituent-binary mixtures. The superior capability of Model PPR-3, compared with the Wilson equation, to represent the excess molar enthalpies of the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture is illustrated in Figures 7.7 - 7.9. It can be seen that Model PPR-3 is capable of predicting the excess molar enthalpies of the ternary mixture more accurately than the Wilson equation with both temperature-dependent and temperature-independent parameters for the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture at 298.15 K with $x_2/(1-x_1-x_2)=0.9989$ and $x_2/(1-x_1-x_2)=2.9752$ whereas the results obtained from Model PPR-3 is not as good as those of the Wilson equation with temperature-dependent parameters but better than those with temperature-

independent parameters for the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture at 298.15 K with $x_2/(1-x_1-x_2)=0.3338$.

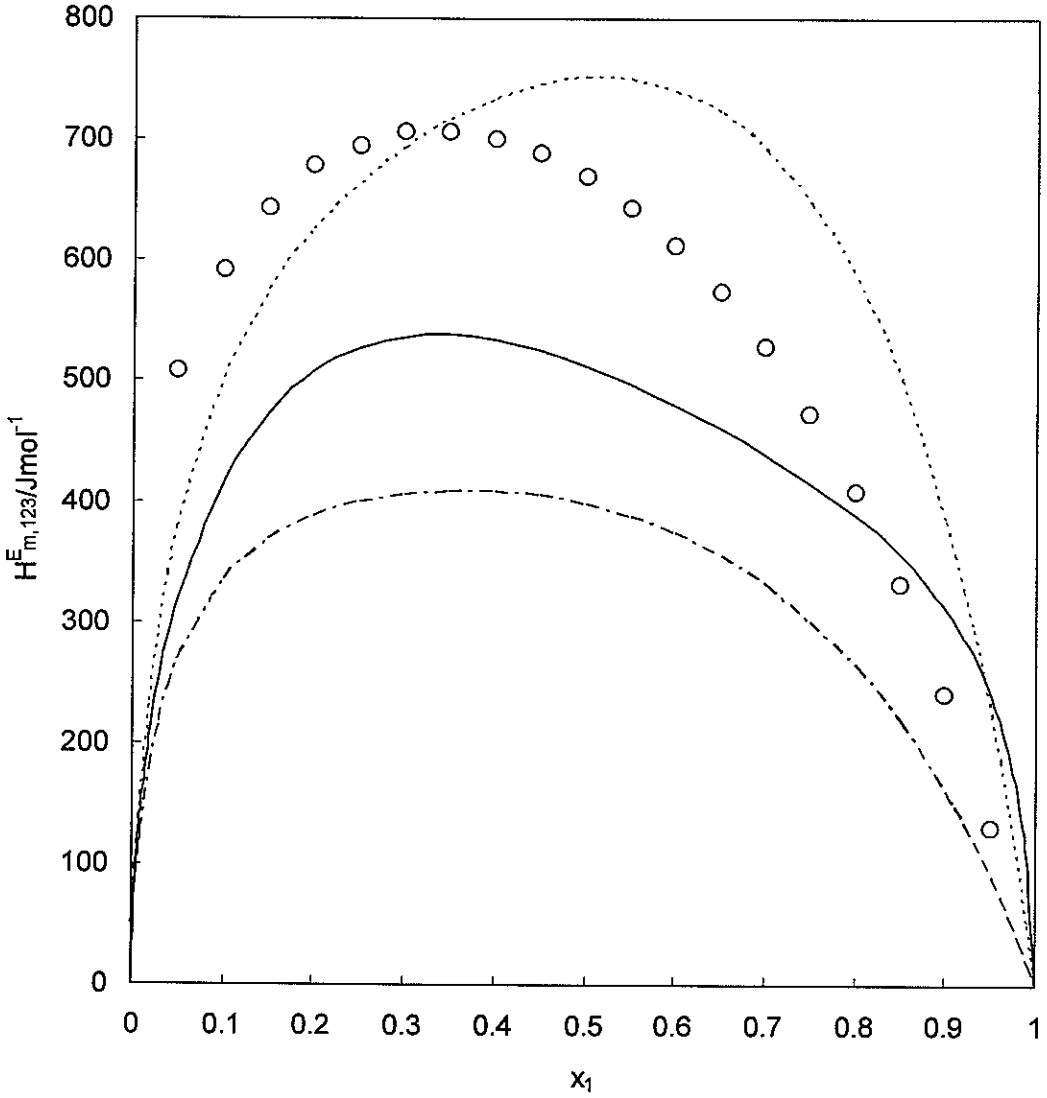

Figure 7.7: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15 K with $x_2/(1-x_1-x_2)=0.3338$. o, Experimental Results; —, Calculated from Model PPR-3; ----, Calculated from the Wilson Equation with Temperature-dependent Parameters in Equations (7.2.7, 7.2.8, 7.2.10, 7.2.11); – – –, Calculated from the Wilson Equation with Temperature-independent Parameters in Table 7.1.

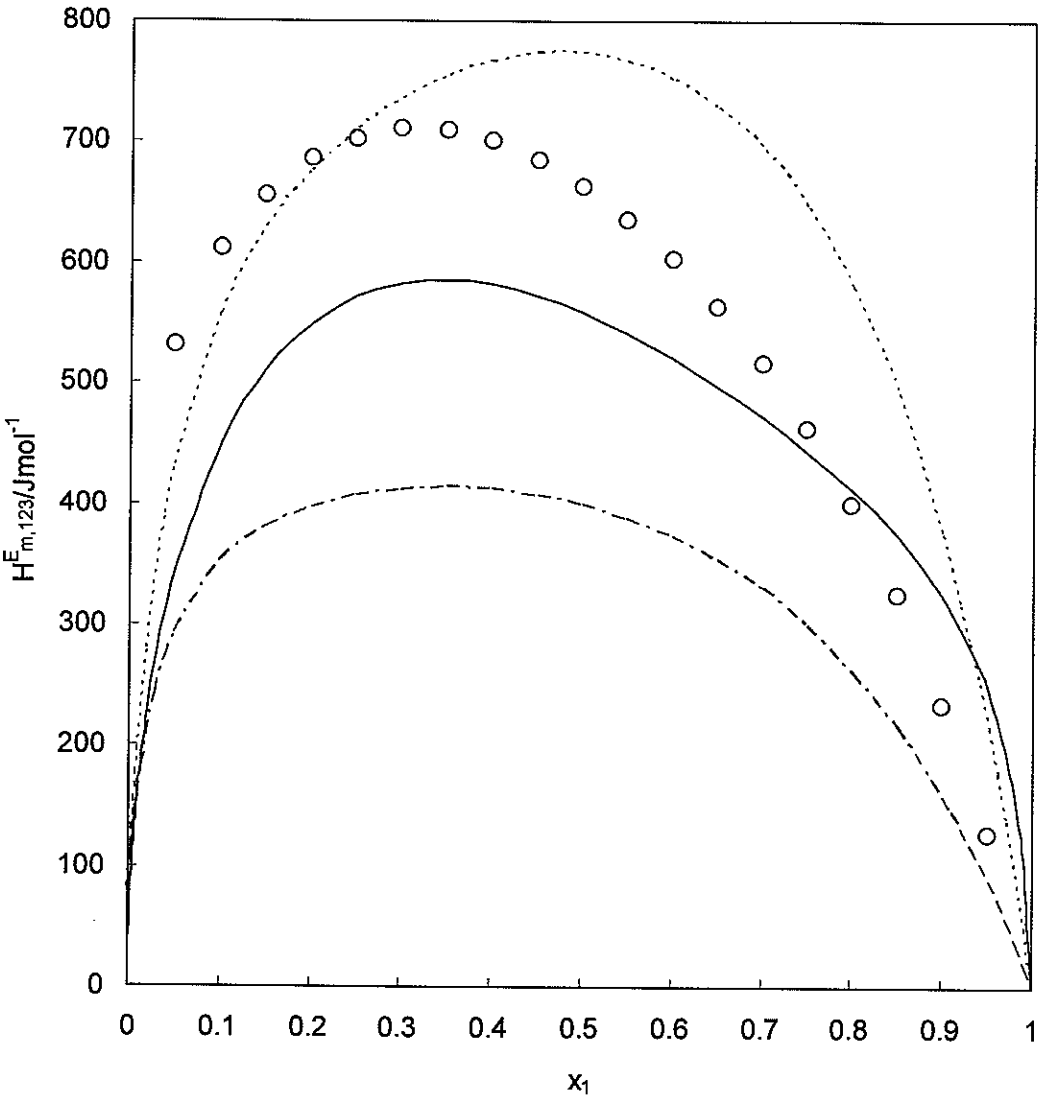

Figure 7.8: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15 K with $x_2/(1-x_1-x_2)=0.9989$. o, Experimental Results; —, Calculated from Model PPR-3; ----, Calculated from the Wilson Equation with Temperature-dependent Parameters in Equations (7.2.7, 7.2.8, 7.2.10, 7.2.11); – – – –, Calculated from the Wilson Equation with Temperature-independent Parameters in Table 7.1.

In addition to the ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture and its constituent-binary mixtures, Model PPR-3 has been used to calculate the excess molar enthalpies of alkanol+hydrocarbon mixtures. The characteristic behavior of H^E is correctly predicted even if quantitative discrepancies with the experimental data are

observed. The predicted H^E results for some selected mixtures are shown in Appendix F.

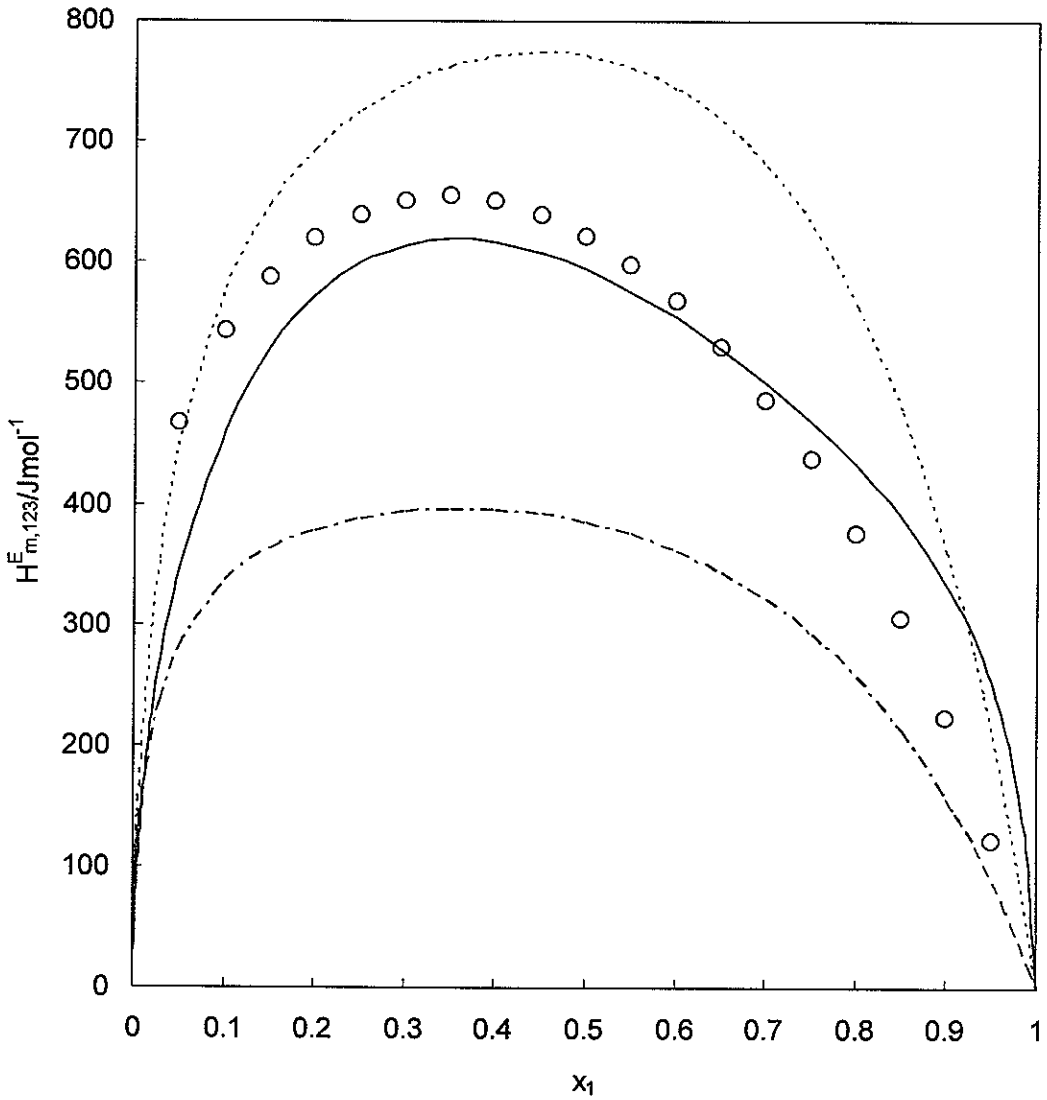

Figure 7.9: Excess Molar Enthalpies for Ethanol(1)+*n*-Hexane(2)+Cyclohexane(3) System at 298.15 K with $x_2/(1-x_1-x_2)=2.9752$. o, Experimental Results; —, Calculated from Model PPR-3; ----, Calculated from the Wilson Equation with Temperature-dependent Parameters in Equations (7.2.7, 7.2.8, 7.2.10, 7.2.11); ----, Calculated from the Wilson Equation with Temperature-independent Parameters in Table 7.1.

CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The infinite linear association model and the monomer-dimer association model have been incorporated into the PR EOS with two different sets of mixing rules to develop four different forms of equations of state for associating systems.

The reformulated PR equations have been successfully used to represent the vapor pressures and liquid densities of pure associating compounds including alkanols, carboxylic acids, water, ketones, as well as nonassociating substances by using the pure compound parameters determined from the experimental data. The vapor pressure and liquid density values calculated by means of the reformulated PR equations are in good agreement with the experimental data reported in the literature. The performance of different forms of the reformulated equations in representing the volumetric properties of pure associating compounds have been compared with that of the Hong-Hu equation (Hong and Hu, 1989) and the AMH equation (Nan *et al.*, 2001a). The comparison serves to show that, in general, Model PPR-3, which is based on the infinite linear association model with the Heidemann and Prausnitz approach to defining mixture parameters, is capable of representing both vapor pressures and liquid densities of pure associating compounds with better accuracy than other reformulated equations, the Hong-Hu equation and the AMH equation. Models PPR-2 and PPR-4, which have been developed on the basis of the monomer-dimer association model with the Hu et al., and Heidemann and Prausnitz approaches to defining mixture parameters, have been shown to be superior to the Hong-Hu equation (Hong and Hu, 1989) in the representation of the vapor pressures of acids. On the other hand, Model PPR-2 and the Hong-Hu equation present comparable results for the correlation of liquid densities of acids whereas Model PPR-4 is incapable of representing the liquid densities of acids with good accuracy when compared with Model PPR-2 and the Hong-Hu equation.

The reformulated PR equations have been extended to VLE calculations of binary systems in which one or both of the components are associating species. The capabilities of the reformulated PR equations are compared with the Hong-Hu equation, the AMH equation and the Wilson equation fitting the binary interaction parameters from the experimental VLE data. On the basis of the results obtained for the selected systems, in general, the reformulated equations with the exception of Model PPR-1 are superior to the Wilson equation for all tested systems except for alkanol+hydrocarbon systems. They are at least as good as the Hong-Hu equation and the AMH equation, although the number of tested systems from Hong and Hu (1989) and Nan *et al.* (2001a) are far less than the number considered in this work.

The excess molar enthalpies of the ethanol+*n*-hexane system at 298.15 K, 303.15 K and 313.15 K and those of the ethanol+cyclohexane system at 298.15 K have been measured in an LKB 2107 microcalorimeter. The reliability of the microcalorimeter is tested by comparing the experimental data measured at 298.15 K and 303.15 K from the present work with those found in the literature. Additionally, new excess molar enthalpy data, measured at 298.15 K, have been reported for the ethanol+*n*-hexane+cyclohexane system. Smooth representations of the results are described and used to construct contours of constant enthalpy on a Roozeboom diagram. Reasonable estimates of the excess molar enthalpies of the three constituent-binary mixtures can be obtained by using both the Liebermann-Fried model and the Flory theory.

An attempt has been made to represent, simultaneously, both VLE and excess enthalpy behavior of the ethanol+*n*-hexane and ethanol+cyclohexane systems by using the Wilson equation and Model PPR-3. Both Model PPR-3 and the Wilson equation are extended to predict the ethanol+*n*-hexane+cyclohexane ternary system at 298.15 K with the binary interaction parameters determined from the experimental VLE data of the three constituent-binary mixtures. The calculated results show that in general, Model PPR-3 is better than or as good as the Wilson equation in predicting the excess molar enthalpies of selected binary and ternary systems involving one associating species. However, quantitative discrepancies with the experimental data are observed.

8.2 Recommendations and Future Work

The reformulated PR equations (Models PPR-2, PPR-3 and PPR-4) have been applied to the VLE calculations of associating systems. For more complex associating systems such as alkanol+carboxyclic acid, the reformulated equations do not fit the experimental data as closely. It can be concluded that neither the monomer-dimer association model nor the infinite linear association model is capable of representing, accurately, the behavior of this kind of associating systems. An appropriate modification, for example, would be used to incorporate multiple association models with the equation of state to provide solutions that are acceptable for engineering application. However, it also should be mentioned that using the different association models to treat the different species in the mixtures would produce more complex equations that require much more computational time.

For alkanol+hydrocarbon systems, the VLE results obtained from the present work are not as satisfactory compared with those calculated from the Wilson equation. The likely, but uncertain reason for the poor results maybe due to the unsuitability of the mixing rules suggested by Heidemann and Prausnitz (1976). More work should be done on formulating new mixing rules for the proposed models.

Further improvement should be made to study mixtures of alkanol+alkanol and alkanol+water. Model development has been completed, but applying it to the phase equilibrium calculations of the systems mentioned above is not carried out due to time limitations. It is anticipated that the equation developed on the basis of the infinite linear association model and the mixing rules suggested by Heidemann and Prausnitz (1976), could be used to represent the phase behavior of alkanol+alkanol and alkanol+water systems with better accuracy. It also should be pointed out that water does not form linear association species but produces three-dimensional clusters. However the infinite linear association model is an approximation only for the self-association and cross-association of alkanols, ringed species or three-dimensional clusters are neglected. Therefore, the developed equation should work well for the alkanol+alkanol systems, not for the alkanol+water systems. A more realistic model for the association of water should be considered to provide estimates of VLE and other thermodynamic data of these systems.

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APPENDIX A
PURE COMPONENT DATABASE

Substance	Formula	MW/g·mol^{-1}	P_c/MPa	T_c/K	ω	A	B	C	D	E
Methylene Chloride	CH2Cl2	84.932	6.08	510	0.1986	101.6	-6541.6	-12.247	1.2311E-05	2
Formaldehyde	CH2O	30.026	6.5861	408	0.2816	101.510	-4917.2	-13.765	2.2031E-02	1
Formic acid	CH2O2	46.026	5.81	588	0.3173	50.323	-5378.2	-4.203	3.4697E-06	2
Methyl Chloride	CH3Cl	50.488	6.68	416.25	0.1531	64.697	-4048.1	-6.8066	1.0371E-05	2
Nitromethane	CH3NO2	61.04	6.3126	588.15	0.3477	87.411	-7133.2	-9.7786	7.9061E-06	2
Methanol	CH4O	32.042	8.0956	512.58	0.5656	109.930	-7472.3	-13.9880	1.5281E-02	1
Acetaldehyde	C2H4O	44.053	5.55	461	0.3167	206.070	-8478.6	-31.5480	4.6314E-02	1
Acetic acid	C2H4O2	60.053	5.7857	592.71	0.4624	70.230	-6846.5	-7.0320	5.0210E-06	2
Ethanol	C2H6O	46.069	6.3835	516.25	0.6371	59.796	-6595.0	-5.0474	6.3000E-07	2
Acrylic acid	C3H4O2	72.064	5.66	615	0.5180	57.992	-7218.0	-4.8813	1.0060E-03	1
Acetone	C3H6O	58.08	4.7015	508.2	0.3064	70.720	-5685.0	-7.3510	6.3000E-06	2
Allyl alcohol	C3H6O	58.08	5.62	545.05	0.5723	61.542	-6913.5	-5.3010	3.2562E-18	6
n-Propionaldehyde	C3H6O	58.08	4.66	496	0.3015	65.137	-5309.5	-6.5289	5.8611E-06	2
Propionic acid	C3H6O2	74.079	5.3702	612	0.5444	72.659	-8101.1	-6.9044	7.1989E-18	6
1-Propanol	C3H8O	60.096	5.1696	536.71	0.6279	77.460	-7960.0	-7.5235	3.0000E-07	2
Isopropanol	C3H8O	60.096	4.7643	508.31	0.6689	92.935	-8177.1	-10.0310	3.9988E-06	2
Butyric acid	C4H8O2	88.106	4.42	628	0.6041	73.191	-8722.3	-6.8627	3.3158E-18	6
Isobutyric acid	C4H8O2	88.106	4.053	609.15	0.6181	64.672	-7952.4	-5.7065	3.6870E-18	6

Substance	Formula	MW/g·mol^{-1}	P_c/MPa	T_c/K	ω	A	B	C	D	E
n-Butane	C4H10	58.123	3.7969	425.18	0.1993	62.570	-4322.0	-6.3640	6.8000E-06	2
1-Butanol	C4H10O	74.123	4.4127	562.93	0.5945	96.230	-9214.3	-10.2950	1.9957E-06	2
Isobutanol	C4H10O	74.123	4.2952	547.73	0.5885	256.520	-14520.0	-36.9470	3.3300E-02	1
2-Butanol	C4H10O	74.123	4.1938	536.01	0.5711	118.750	-9783.0	-13.7930	5.0630E-06	2
Tert-butanol	C4H10O	74.123	3.9719	506.2	0.6158	170.260	-11505.0	-21.8050	1.3412E-05	2
Pentanoic acid	C5H10O2	102.133	3.81	651	0.6269	85.300	-9925.2	-8.5175	3.3335E-18	6
Isopentanoic acid	C5H10O2	102.133	3.89	634	0.6480	88.183	-9843.0	-8.9691	5.9268E-18	6
n-Pentane	C5H12	72.15	3.3688	469.65	0.2486	81.624	-5578.5	-9.2354	9.4522E-06	2
1-Pentanol	C5H12O	88.15	3.88	586.15	0.5938	168.960	-12659.0	-21.3660	1.1591E-05	2
Isoamyl alcohol	C5H12O	88.15	3.88	579.45	0.5558	109.750	-10394.0	-12.0830	6.2013E-18	6
Benzene	C6H6	78.114	4.898	562.16	0.2108	78.050	-6275.5	-8.4443	6.2600E-06	2
Cyclohexane	C6H12	84.161	4.0748	553.54	0.2118	125.410	-7367.0	-17.0070	1.9050E-02	1
Hexanoic acid	C6H12O2	116.16	3.35	667.00	0.6701	133.160	-13033.0	-15.4580	4.3099E-06	2
n-Hexane	C6H14	86.177	3.0123	507.43	0.3046	165.470	-8353.3	-23.9270	2.9496E-02	1
Isohexane	C6H14	86.177	3.0103	497.50	0.2781	75.692	-5730.7	-8.2295	7.4608E-06	2
3-Methy pentane	C6H14	86.177	3.124	504.43	0.2772	103.150	-6757.3	-12.5470	1.2920E-05	2
2,2-Dimethyl butane	C6H14	86.177	3.0806	488.78	0.2339	81.174	-5647.6	-9.2016	9.6144E-06	2
1-Hexanol	C6H14O	102.177	3.51	611.35	0.5803	129.160	-11398.0	-15.1990	5.4449E-06	2

Substance	Formula	MW/g·mol^{-1}	P_c/MPa	T_c/K	ω	A	B	C	D	E
Toluene	C7H8	92.141	4.1086	591.79	0.2641	83.359	-6995.0	-9.1635	6.2250E-06	2
Heptanoic acid	C7H14O2	130.187	2.99	680.00	0.7173	470.030	-26685.0	-69.9410	5.9250E-02	1
n-Heptane	C7H16	100.204	2.7358	540.26	0.3511	166.830	-9155.5	-23.7620	2.6787E-02	1
2-Methyl hexane	C7H16	100.204	2.7338	530.37	0.3282	129.480	-7779.3	-17.5470	1.9018E-02	1
1-Heptanol	C7H16O	116.203	3.15	631.90	0.5874	160.080	-14095.0	-19.2110	1.7043E-17	6
Ethyl benzene	C8H10	106.167	3.6094	617.17	0.3036	88.246	-7691.1	-9.7970	5.9310E-06	2
m-Xylene	C8H10	106.167	3.5412	617.05	0.3260	84.747	-7594.1	-9.2570	5.5500E-06	2
o-Xylene	C8H10	106.167	3.7342	630.37	0.3127	90.644	-7960.8	-10.1260	6.0150E-06	2
p-Xylene	C8H10	106.167	3.5108	616.26	0.3259	143.170	-9247.0	-19.4410	1.9084E-02	1
Octanoic acid	C8H16O2	144.214	2.69	692.00	0.7792	260.170	-18781.0	-36.0880	2.5679E-02	1
n-Octane	C8H18	114.231	2.4863	568.83	0.3962	71.886	-6933.9	-7.2653	3.3802E-06	2
1-Octanol	C8H18O	130.23	2.86	652.50	0.5944	156.230	-14300.0	-18.5900	1.3320E-17	6
Nonanoic acid	C9H18O2	158.241	2.45	703.00	0.8308	236.920	-19451.0	-30.6620	1.3076E-05	2
n-Nonane	C9H20	128.258	2.3056	595.65	0.4377	66.184	-7237.0	-6.2614	1.6686E-06	2
n-Decane	C10H22	142.285	2.1229	618.45	0.4842	65.940	-7733.1	-6.1174	1.1180E-06	2
Decanol	C10H22O	158.284	2.37	690.00	0.6134	242.130	-18772.0	-31.6410	1.3892E-05	2
Dodecanoic acid	C12H24O2	200.321	1.94	734.00	0.9671	204.560	-20612.0	-24.7800	9.6813E-18	6
Dodecanol	C12H26O	186.338	1.93	721.00	0.6393	268.640	-21198.0	-35.2750	1.4172E-05	2
Water	H2O	18.015	22.055	647.13	0.3449	73.649	-7258.2	-7.3037	4.1653E-06	2

APPENDIX B
FORTRAN PROGRAM

B1. Calculations of Thermodynamic Properties of Pure Associating Compounds from the Four Models

Model PPR-1:

```
C     This program allows you to calculate the vapor pressure and
C     liquid density using Model PPR-1
C     Prepared by Jianyuan Pang

C     *****************Beginning of Main Program*********************
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer sym
      Dimension tt(50),T(50),p(50),pexp(50),roulexp(50),vl(50)
      Dimension a(50),AA(50),BB(50),vvv(50),vvl(50),phiv(50),phil(50)
      Dimension ratio(50),errorp(50),errorl(50),K(50)
      Dimension nrv(50),nrl(50),z1L(50),z1V(50)
      Dimension fl(50),fv(50),gl(50),gv(50)
      open(16,file='input.txt',status='old')
c     open(16,file='input2.txt',status='old')
      open(17,file='output.txt',status='old')
c     read(16,*) e1,e2,e3,e4,e5
      read(16,*) N,C1,C2,aa1,aa2,b,w
      read(16,*) (tt(i),pexp(i),i=1,N)
c     read(16,*) (tt(i),roulexp(i),i=1,N)
      R=0.08314
      write(*,*)'Comparision of calculated results with experimental
     $data
      write(*,*) 't/C      pexp      pcal     err(%)   roule    roulc
     $err(%)'
      write(*,*)  '          bar       bar              kg/m^3  kg/m^3'
      do 52 i=1,N
c     vl(i)=w/rouLexp(i)
      T(i)=tt(i)+273.15
      a(i)=(aa1+aa2*T(i))**2.
c     pexp(i)=exp(e1+e2/T(i)+e3*log(T(i))+e4*T(i)**e5)/1e5
      p(i)=pexp(i)
      K(i)=exp(C1/T(i)+C2)
7     BB(i)=b*p(i)/R/T(i)
      AA(i)=a(i)*p(i)/(R*T(i))**2.0
      AVL=AA(i)
      BVL=BB(i)
      KK=K(i)
      pp=p(i)
C     Calculate compressiblity factor for vapor phase
      sym=2
      Call NEWRAP(AVL,BVL,KK,pp,ZV,sym)
      vvv(i)=ZV*R*T(i)/p(i)
C     Calculate compressiblity factor for liquid phase
      sym=1
      Call NEWRAP(AVL,BVL,KK,pp,ZL,sym)
      vvl(i)=ZL*R*T(i)/p(i)
      gl(i)=((ZL+(1.+sqrt(2.))*BB(i))/(ZL+(1.-sqrt(2.))*BB(i)))
```

```
     $     **(AA(i)/BB(i)/2./sqrt(2.))
           gv(i)=((ZV+(1.+sqrt(2.))*BB(i))/(ZV+(1.-sqrt(2.))*BB(i)))
     $     **(AA(i)/BB(i)/2./sqrt(2.))
C          nrl -- nT/n0 for liquid; nrv -- nT/n0 for vapor from equation
           nrl(i)=2.0/(1.0+sqrt(1.0+4.0*K(i)*R*T(i)/(vvl(i)-b)/gl(i)))
           nrv(i)=2.0/(1.0+sqrt(1.0+4.0*K(i)*R*T(i)/(vvv(i)-b)/gv(i)))
C          calculate liquid fugacity coefficent phi from equation
           b1=-log(1-b/vvl(i))
           b2=b*nrl(i)/(vvl(i)-b)
           b3=-a(i)*vvl(i)*nrl(i)/R/T(i)/(vvl(i)**2.+2.*b*vvl(i)-b**2.)
           b4=a(i)/2./sqrt(2.)/b/R/T(i)*log((vvl(i)+b-sqrt(2.0)*b)
     $     /(vvl(i)+b+sqrt(2.)*b))
           b5=-log(p(i)*vvl(i)/nrl(i)/R/T(i))
           phil(i)=exp(b1+b2+b3+b4+b5)
           z1L(i)=nrl(i)
           fl(i)=phil(i)*z1L(i)*p(i)
C          calculate vapor fugacity coefficent phi from equation
           a1=-log(1-b/vvv(i))
           a2=b*nrv(i)/(vvv(i)-b)
           a3=-a(i)*vvv(i)*nrv(i)/R/T(i)/(vvv(i)**2.+2.*b*vvv(i)-b**2.)
           a4=a(i)/2./sqrt(2.)/b/R/T(i)*log((vvv(i)+b-sqrt(2.0)*b)
     $          /(vvv(i)+b+sqrt(2.)*b))
           a5=-log(p(i)*vvv(i)/nrv(i)/R/T(i))
           phiv(i)=exp(a1+a2+a3+a4+a5)
           z1V(i)=nrv(i)
           fv(i)=phiv(i)*z1V(i)*p(i)
           ratio(i)=abs(fl(i)/fv(i)-1)
           IF (ratio(i).GT.1.e-4) then
           p(i)=p(i)*fl(i)/fv(i)
           GOTO 7
           ENDIF
           errorp(i)=(p(i)-pexp(i))/pexp(i)*100.
c          calculate roulexp
c          errorl(i)=(1./vvl(i)-1./vl(i))*vl(i)*100.
c          write(*,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c          $     w/vvl(i),errorl(i)
c          write(17,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c          $     w/vvl(i),errorl(i)
c          calculate pexp
           write(*,59) tt(i),pexp(i),p(i),errorp(i)
           write(17,59) tt(i),pexp(i),p(i),errorp(i)
59         format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2)
52         continue
           errp=0.
           errl=0.
           AADp=0.
           AADrou=0.
           do 55 i=1,N
           AADp=AADp+abs(errorp(i))
           AADrou=AADrou+abs(errorl(i))
55         errp=errp+errorp(i)**2.
           errl=errl+errorl(i)**2.
           AADp=AADp/N
           AADrou=AADrou/N
           rms=sqrt(errp/N+errl/N)
           write(*,*) ' C1       C2       a1       a2       b1/lmol-1  AADP(%)
          $AADL(%)'
```

```
      write(*,56) C1,C2,aa1,aa2,b,AADp,AADrou
      write(17,*) ' C1      C2      a1      a2      b1/lmol-1
      AADP(%)
     $AADL(%)'
      write(17,56) C1,C2,aa1,aa2,b,AADp,AADrou
51    format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2,3x,f7.2,2x,f7.2,1x,f6.2)
56    format(1x,f5.0,1x,f8.4,1x,f7.4,1x,f8.5,2x,f8.5,2x,f6.2,5x,f6.2)
      end

*********************NEWTON - RAPHSON METHOD*****************************
*     THIS PROGRAM FINDS THE ROOT OF AN ALGEBRAIC AND TRANSCENDENTAL  *
*                    EQUATION BY NEWTON-RAPHSON METHOD                *
*********************************************************************
      SUBROUTINE NEWRAP(AVL,BVL,KK,PP,xx,sym)
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer maxi,i,sym
c     Defining the Function 'F(xx)=0' to be solved
      F(xx)=2./(1.+sqrt(1.+4.*KK*PP/(xx-BVL)/((xx+(1.+sqrt(2.))*BVL)
     $ /(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2./sqrt(2.))))
     $ *(1./(xx-BVL)-AVL/(xx**2.+2.0*BVL*xx-BVL**2.0))-1.
c     Defining the Function for derivative of 'F(xx)'
      DER(xx)=2./(1.+sqrt(1.+4.*KK*PP/(xx-BVL)/((xx+(1.+sqrt(2.))*BVL)
     $ /(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2./sqrt(2.))))
     $*(-1./(xx-BVL)**2.+2.*AVL*(xx+BVL)/(xx**2.+2.*BVL*xx-BVL**2.)
     $**2.)-4.0*KK*PP/(1.+sqrt(1.+4*KK*PP/(xx-BVL)
     $/((xx+(1.+sqrt(2.))*BVL)
     $ /(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2./sqrt(2.))))**2.
     $ /sqrt(1.+4*KK*PP/(xx-BVL)/((xx+(1.+sqrt(2.))*BVL)
     $ /(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2./sqrt(2.)))
     $ *(AVL/(xx-BVL)/(xx+BVL-sqrt(2.)*BVL)/(xx+BVL+sqrt(2.)*BVL)
     $ /((xx+(1.+sqrt(2.))*BVL)/(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2.
     $/sqrt(2.))-1./(xx-BVL)**2./((xx+(1.+sqrt(2.))*BVL)
     $ /(xx+(1.-sqrt(2.))*BVL))**(AVL/BVL/2./sqrt(2.)))*(1./(xx-BVL)
     $ -AVL/(xx**2.+2.*BVL*xx-BVL**2.))
      IF (sym.EQ.1) THEN
      xini=1.001*BVL
      ELSEif (sym.eq.2) then
      xini=0.9
      ENDIF
      es=1.e-8
      maxi=1.e+7
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
      write(*,*) 'The root is not reached within the error limit after
     $ prescribed number of iteration.'
```

```
      write(*,*)
      write(*,*) 'The approximate root =',xini
      write(*,*)
      write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
      write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end
```

Model PPR-2:

```
C     This program allows you to calculate the vapor pressure and
C     liquid density using Model PPR-2
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer sym
      Dimension tt(50),T(50),p(50),pexp(50),roulexp(50),vl(50)
      Dimension a(50),AA(50),BB(50),vvv(50),vvl(50),phiv(50),phil(50)
      Dimension ratio(50),errorp(50),errorl(50),K(50)
      Dimension nrv(50),nrl(50),z1L(50),z1V(50)
      Dimension fl(50),fv(50),wl(50),wv(50)
      open(16,file='input.txt',status='old')
c     open(16,file='input2.txt',status='old')
      open(17,file='output.txt',status='old')
c     read(16,*) e1,e2,e3,e4,e5
      read(16,*) N,C1,C2,aa1,aa2,b,w
      read(16,*) (tt(i),pexp(i),i=1,N)
c     read(16,*) (tt(i),roulexp(i),i=1,N)
      R=0.08314
      write(*,*)'Comparision of calculated results with experimental
     $data
      write(*,*) 't/C      pexp      pcal    err(%)   roule    roulc
     $err(%)'
      write(*,*)  '          bar       bar              kg/m^3  kg/m^3'
      do 52 i=1,N
c     vl(i)=w/rouLexp(i)
      T(i)=tt(i)+273.15
      a(i)=(aa1+aa2*T(i))**2.
c     pexp(i)=exp(e1+e2/T(i)+e3*log(T(i))+e4*T(i)**e5)/1e5
      p(i)=pexp(i)
      K(i)=exp(C1/T(i)+C2)
7     BB(i)=b*p(i)/R/T(i)
      AA(i)=a(i)*p(i)/(R*T(i))**2.0
      AVL=AA(i)
      BVL=BB(i)
      KK=K(i)
      pp=p(i)
      sym=2
      Call NEWRAP(AVL,BVL,KK,pp,ZV,sym)
      vvv(i)=ZV*R*T(i)/p(i)
      sym=1
      Call NEWRAP(AVL,BVL,KK,pp,ZL,sym)
      vvl(i)=ZL*R*T(i)/p(i)
      wl(i)=K(i)*R*T(i)/vvl(i)*exp(-log(1.-b/vvl(i))+a(i)/b/R/T(i)/2.
     $ /sqrt(2.)*log((vvl(i)+(1.-qrt(2.))*b)/(vvl(i)+(1.+sqrt(2.))*b)))
      nrl(i)=2.0*(wl(i)-1.)/(4.0*wl(i)-1.-sqrt(1+8.*wl(i)))
      b1=-log(1-b/vvl(i))
```

```
      b2=b*nrl(i)/(vvl(i)-b)
      b3=a(i)/R/T(i)/b/2./sqrt(2.)*log((vvl(i)+(1.-sqrt(2.))*b)
     $      /(vvl(i)+(1.+sqrt(2.))*b))
      b4=-nrl(i)*a(i)*vvl(i)/R/T(i)/(vvl(i)**2.+2.*b*vvl(i)-b**2.)
      b5=-log(p(i)*vvl(i)/nrl(i)/R/T(i))
      phil(i)=exp(b1+b2+b3+b4+b5)
      z1L(i)=(-3.+sqrt(1+8.*wl(i)))/2./(wl(i)-1.)
      fl(i)=phil(i)*z1L(i)*p(i)
      wv(i)=K(i)*R*T(i)/vvv(i)*exp(-log(1.-b/vvv(i))+a(i)/b/R/T(i)/2.
     $ /sqrt(2.)*log((vvv(i)+(1.-qrt(2.))*b)/(vvv(i)+(1.+sqrt(2.))*b)))
      nrv(i)=2.0*(wv(i)-1.)/(4.0*wv(i)-1.-sqrt(1+8.*wv(i)))
      a1=-log(1-b/vvv(i))
      a2=b*nrv(i)/(vvv(i)-b)
      a3=a(i)/R/T(i)/b/2./sqrt(2.)*log((vvv(i)+(1.-sqrt(2.))*b)
     $      /(vvv(i)+(1.+sqrt(2.))*b))
      a4=-nrv(i)*a(i)*vvv(i)/R/T(i)/(vvv(i)**2.+2.*b*vvv(i)-b**2.)
      a5=-log(p(i)*vvv(i)/nrv(i)/R/T(i))
      phiv(i)=exp(a1+a2+a3+a4+a5)
      z1V(i)=(-3.+sqrt(1+8.*wv(i)))/2./(wv(i)-1.)
      fv(i)=phiv(i)*z1V(i)*p(i)
      ratio(i)=abs(fl(i)/fv(i)-1)
      IF (ratio(i).GT.1.e-4) then
      p(i)=p(i)*fl(i)/fv(i)
      GOTO 7
      ENDIF
      errorp(i)=(p(i)-pexp(i))/pexp(i)*100.
c     errorl(i)=(1./vvl(i)-1./vl(i))*vl(i)*100.
c     write(*,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c     $     w/vvl(i),errorl(i)
c     write(17,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c     $     w/vvl(i),errorl(i)
      write(*,59) tt(i),pexp(i),p(i),errorp(i)
      write(17,59) tt(i),pexp(i),p(i),errorp(i)
59    format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2)
52    continue
      errp=0.
      errl=0.
      AADp=0.
      AADrou=0.
      do 55 i=1,N
      AADp=AADp+abs(errorp(i))
      AADrou=AADrou+abs(errorl(i))
55    errp=errp+errorp(i)**2.
      errl=errl+errorl(i)**2.
      AADp=AADp/N
      AADrou=AADrou/N
      rms=sqrt(errp/N+errl/N)
      write(*,*) ' C1      C2      a1      a2      b1/lmol-1  AADP(%)
     $AADL(%)'
      write(*,56) C1,C2,aa1,aa2,b,AADp,AADrou
      write(17,*) ' C1      C2      a1      a2      b1/lmol-1
      AADP(%)
     $AADL(%)'
      write(17,56) C1,C2,aa1,aa2,b,AADp,AADrou
51    format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2,3x,f7.2,2x,f7.2,1x,f6.2)
56    format(1x,f5.0,1x,f8.4,1x,f7.4,1x,f8.5,2x,f8.5,2x,f6.2,5x,f6.2)
      end
```

```
      SUBROUTINE NEWRAP(AVL,BVL,KK,PP,xx,sym)
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer maxi,i,sym
      F(xx)=1-2.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)
     $ /(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.))-1.)
     $ /(4.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $ **(A/B/2./sqrt(2.)))-1.-sqrt(1.+8.*(KK*PP/(xx-B)*
     $ ((xx+(1.-qrt(2.))*B)/(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.)))))
     $       *(1./(xx-B)-A/(xx**2.+2.*B*xx-B**2.))
      DER(xx)=2.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)
     $ /(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.))-1.)
     $ /(4.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $  **(A/B/2./sqrt(2.)))-1.-sqrt(1.+8.*(KK*PP/(xx-B)
     $ *((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $ **(A/B/2./sqrt(2.)))))
     $ *(1./(xx-B)**2.-2.*A*(xx+B)/(xx**2.+2.*B*xx-B**2.)**2.)
     $ -(1./(xx-B)-A/(xx**2.+2.*B*xx-B**2.))
     $ *(6.-2.*sqrt(1.+8.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)
     $ /(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.))))
     $ +8.*((KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $ **(A/B/2./sqrt(2.)))-1.)/sqrt(1.+8.*(KK*PP/(xx-B)
     $ *((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $ **(A/B/2./sqrt(2.)))))/(4.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)
     $ /(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.)))-1.
     $ -sqrt(1.+8.*(KK*PP/(xx-B)*((xx+(1.-sqrt(2.))*B)
     $ /(xx+(1.+sqrt(2.))*B))**(A/B/2./sqrt(2.)))))**2.
     $ *(-KK*PP/(xx-B)**2.*((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $  **(A/B/2./sqrt(2.))+KK*PP*A/(xx-B)/(xx+(1.+sqrt(2.))*B)**2.
     $  *((xx+(1.-sqrt(2.))*B)/(xx+(1.+sqrt(2.))*B))
     $  **(A/B/2./sqrt(2.)-1.))
      IF (sym.EQ.1) THEN
      xini=1.001*BVL
      ELSEif (sym.eq.2) then
      xini=0.9
      ENDIF
      es=1.e-8
      maxi=1.e+7
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
      write(*,*) 'The root is not reached within the error limit after
     $ prescribed number of iteration.'
      write(*,*)
      write(*,*) 'The approximate root =',xini
      write(*,*)
```

```
      write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
      write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end
```

Model PPR-3:

```
C     This program allows you to calculate the vapor pressure and
C     liquid density using Model PPR-3
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer sym
      Dimension tt(50),T(50),p(50),pexp(50),roulexp(50),vl(50)
      Dimension a(50),AA(50),BB(50),vvv(50),vvl(50),phiv(50),phil(50)
      Dimension ratio(50),errorp(50),errorl(50),K(50)
      Dimension nrv(50),nrl(50),z1L(50),z1V(50)
      Dimension fl(50),fv(50)
      open(16,file='input.txt',status='old')
c     open(16,file='input2.txt',status='old')
      open(17,file='output.txt',status='old')
c     read(16,*) e1,e2,e3,e4,e5
      read(16,*) N,C1,C2, aa1,aa2,aa3,bb1,bb2,w
      read(16,*) (tt(i),pexp(i),i=1,N)
c     read(16,*) (tt(i),roulexp(i),i=1,N)
      R=0.08314
      write(*,*)'Comparision of calculated results with experimental
     $data
      write(*,*) 't/C      pexp      pcal    err(%)   roule    roulc
     $err(%)'
      write(*,*)  '         bar       bar              kg/m^3  kg/m^3'
      do 52 i=1,N
c     vl(i)=w/rouLexp(i)
      T(i)=tt(i)+273.15
      a(i)=aa1+aa2*sqrt(T(i))+aa3*T(i)
      b(i)=(bb1+bb2*sqrt(T(i)))**2.
      K(i)=exp(C1/T(i)+C2)
c     pexp(i)=exp(e1+e2/T(i)+e3*log(T(i))+e4*T(i)**e5)/1e5
      p(i)=pexp(i)
7     BB(i)=b(i)*p(i)/R/T(i)
      AA(i)=a(i)*p(i)/(R*T(i))**2.0
      AVL=AA(i)
      BVL=BB(i)
      KK=K(i)
      pp=p(i)
      sym=2
      Call NEWRAP(AVL,BVL,KK,pp,ZV,sym)
      vvv(i)=ZV*R*T(i)/p(i)
      sym=1
      Call NEWRAP(AVL,BVL,KK,pp,ZL,sym)
      vvl(i)=ZL*R*T(i)/p(i)
      nrl(i)=2.0/(1.0+sqrt(1.0+4.0*K(i)*R*T(i)/(vvl(i)-b(i))))
      nrv(i)=2.0/(1.0+sqrt(1.0+4.0*K(i)*R*T(i)/(vvv(i)-b(i))))
      b1=-Log(1.-b(i)/vvL(i))
      b2=b(i)*nrL(i)/(vvL(i)-b(i))
      b3=-a(i)*vvL(i)/R/T(i)/(vvL(i)**2.+2.*b(i)*vvL(i)-b(i)**2.)
      b4=a(i)/2./sqrt(2.)/b(i)/R/T(i)*Log((vvL(i)+b(i)-sqrt(2.0)*b(i))
```

```
     $   /(vvL(i)+b(i)+sqrt(2.)*b(i)))
      b5=-Log(p(i)*vvL(i)/nrL(i)/R/T(i))
      phiL(i)=exp(b1+b2+b3+b4+b5)
      z1L(i)=nrL(i)
      fL(i)=phiL(i)*z1L(i)*p(i)
      a1=-Log(1.-b(i)/vvv(i))
      a2=b(i)*nrv(i)/(vvv(i)-b(i))
      a3=-a(i)*vvv(i)/R/T(i)/(vvv(i)**2.+2.*b(i)*vvv(i)-b(i)**2.)
      a4=a(i)/2./sqrt(2.)/b(i)/R/T(i)*Log((vvv(i)+b(i)-sqrt(2.0)*b(i))
     $      /(vvv(i)+b(i)+sqrt(2.)*b(i)))
      a5=-Log(p(i)*vvv(i)/nrv(i)/R/T(i))
      phiv(i)=exp(a1+a2+a3+a4+a5)
      z1V(i)=nrv(i)
      fv(i)=phiv(i)*z1V(i)*p(i)
      ratio(i)=abs(fl(i)/fv(i)-1)
      IF (ratio(i).GT.1.e-4) then
      p(i)=p(i)*fl(i)/fv(i)
      GOTO 7
      ENDIF
      errorp(i)=(p(i)-pexp(i))/pexp(i)*100.
c     errorl(i)=(1./vvl(i)-1./vl(i))*vl(i)*100.
c     write(*,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c     $     w/vvl(i),errorl(i)
c     write(17,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c     $     w/vvl(i),errorl(i)
      write(*,59) tt(i),pexp(i),p(i),errorp(i)
      write(17,59) tt(i),pexp(i),p(i),errorp(i)
59    format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2)
52    continue
      errp=0.
      errl=0.
      AADp=0.
      AADrou=0.
      do 55 i=1,N
      AADp=AADp+abs(errorp(i))
      AADrou=AADrou+abs(errorl(i))
55    errp=errp+errorp(i)**2.
      errl=errl+errorl(i)**2.
      AADp=AADp/N
      AADrou=AADrou/N
      rms=sqrt(errp/N+errl/N)
      write(*,*) ' C1      C2      a1      a2      b1/lmol-1  AADP(%)
     $AADL(%)'
      write(*,56) C1,C2,aa1,aa2,b,AADp,AADrou
      write(17,*) ' C1      C2      a1      a2      b1/lmol-1
      AADP(%)
     $AADL(%)'
      write(17,56) C1,C2,aa1,aa2,b,AADp,AADrou
51    format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2,3x,f7.2,2x,f7.2,1x,f6.2)
56    format(1x,f5.0,1x,f8.4,1x,f7.4,1x,f8.5,2x,f8.5,2x,f6.2,5x,f6.2)
      end

      SUBROUTINE NEWRAP(AVL,BVL,KK,PP,xx,sym)
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer maxi,i,sym
      F(xx)=1-2./(1.+sqrt(1.+4.*KK*PP/(xx-B)))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
```

```
      DER(xx)=2./(1.+sqrt(1.+(4.*KK*PP/(xx-B))))
     $       /(xx-B)**2.0-4.0*KK*PP/(xx-B)**3.0
     $       /(1.+sqrt(1.+4.*KK*PP/(xx-B)))**2.0
     $       /sqrt(1.+4.*KK*PP/(xx-B))-2.0*A*(xx+B)
     $       /(xx**2.0+2*B*xx-B**2.0)**2.
      IF (sym.EQ.1) THEN
      xini=1.001*BVL
      ELSEif (sym.eq.2) then
      xini=0.9
      ENDIF
      es=1.e-8
      maxi=1.e+7
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
      write(*,*) 'The root is not reached within the error limit after
     $ prescribed number of iteration.'
      write(*,*)
      write(*,*) 'The approximate root =',xini
      write(*,*)
      write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
      write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end
```

Model PPR-4:

```
C     This program allows you to calculate the vapor pressure and
C     liquid density using Model PPR-4
      IMPLICIT REAL*8(A-H,K,N,O-Z)
      integer sym
      Dimension tt(50),T(50),p(50),pexp(50),roulexp(50),vl(50)
      Dimension a(50),AA(50),BB(50),vvv(50),vvl(50),phiv(50),phil(50)
      Dimension ratio(50),errorp(50),errorl(50),K(50)
      Dimension nrv(50),nrl(50),z1L(50),z1V(50)
      Dimension fl(50),fv(50)
      open(16,file='input.txt',status='old')
c     open(16,file='input2.txt',status='old')
      open(17,file='output.txt',status='old')
c     read(16,*) e1,e2,e3,e4,e5
      read(16,*) N,C1,C2, aa1,aa2,aa3,b,w
      read(16,*) (tt(i),pexp(i),i=1,N)
c     read(16,*) (tt(i),roulexp(i),i=1,N)
      R=0.08314
```

```
      write(*,*)'Comparision of calculated results with experimental
     $data
      write(*,*) 't/C      pexp      pcal    err(%)   roule    roulc
     $err(%)'
      write(*,*)  '         bar       bar              kg/m^3  kg/m^3'
      do 52 i=1,N
c     vl(i)=w/rouLexp(i)
      T(i)=tt(i)+273.15
      a(i)=aa1+aa2*sqrt(T(i))+aa3*T(i)
      K(i)=exp(C1/T(i)+C2)
c     pexp(i)=exp(e1+e2/T(i)+e3*log(T(i))+e4*T(i)**e5)/1e5
      p(i)=pexp(i)
7     BB(i)=b*p(i)/R/T(i)
      AA(i)=a(i)*p(i)/(R*T(i))**2.0
      AVL=AA(i)
      BVL=BB(i)
      KK=K(i)
      pp=p(i)
      sym=2
      Call NEWRAP(AVL,BVL,KK,pp,ZV,sym)
      vvv(i)=ZV*R*T(i)/p(i)
      sym=1
      Call NEWRAP(AVL,BVL,KK,pp,ZL,sym)
      vvl(i)=ZL*R*T(i)/p(i)
      nrl(i)=2.0*(K(i)*R*T(i)/(vvl(i)-b)-1.)/(4.0*K(i)*R*T(i)/(vvl(i)
     $-b)-1.-sqrt(1+8.*K(i)*R*T(i)/(vvl(i)-b)))
      nrv(i)=2.0*(K(i)*R*T(i)/(vvv(i)-b)-1.)/(4.0*K(i)*R*T(i)/(vvv(i)
     $-b)-1.-sqrt(1+8.*K(i)*R*T(i)/(vvv(i)-b)))
      b1=-Log(1.-b/vvL(i))
      b2=b(i)*nrL(i)/(vvL(i)-b(i))
      b3=-a(i)*vvL(i)/R/T(i)/(vvL(i)**2.+2.*b*vvL(i)-b**2.)
      b4=a(i)/2./sqrt(2.)/b/R/T(i)*Log((vvL(i)+b-sqrt(2.0)*b)
     $   /(vvL(i)+b+sqrt(2.)*b))
      b5=-Log(p(i)*vvL(i)/nrL(i)/R/T(i))
      phiL(i)=exp(b1+b2+b3+b4+b5)
      z1L(i)=(-3.+sqrt(1+8.*K(i)*R*T(i)/(vvl(i)-b)))/2.
     $      /(K(i)*R*T(i)/(vvl(i)-b)-1.)
      fL(i)=phiL(i)*z1L(i)*p(i)
      a1=-Log(1.-/vvv(i))
      a2=b*nrv(i)/(vvv(i)-b)
      a3=-a(i)*vvv(i)/R/T(i)/(vvv(i)**2.+2.*b*vvv(i)-b**2.)
      a4=a(i)/2./sqrt(2.)/b/R/T(i)*Log((vvv(i)+b-sqrt(2.0)*b)
     $      /(vvv(i)+b+sqrt(2.)*b))
      a5=-Log(p(i)*vvv(i)/nrv(i)/R/T(i))
      phiv(i)=exp(a1+a2+a3+a4+a5)
      z1V(i)=(-3.+sqrt(1+8.*K(i)*R*T(i)/(vvv(i)-b)))/2.
     $      /(K(i)*R*T(i)/(vvv(i)-b)-1.)
      fv(i)=phiv(i)*z1V(i)*p(i)
      ratio(i)=abs(fl(i)/fv(i)-1)
      IF (ratio(i).GT.1.e-4) then
      p(i)=p(i)*fl(i)/fv(i)
      GOTO 7
      ENDIF
      errorp(i)=(p(i)-pexp(i))/pexp(i)*100.
c     errorl(i)=(1./vvl(i)-1./vl(i))*vl(i)*100.
c     write(*,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c     $     w/vvl(i),errorl(i)
```

```
c      write(17,51) tt(i),pexp(i),p(i),errorp(i),w/vl(i),
c      $     w/vvl(i),errorl(i)
       write(*,59) tt(i),pexp(i),p(i),errorp(i)
       write(17,59) tt(i),pexp(i),p(i),errorp(i)
59     format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2)
52     continue
       errp=0.
       errl=0.
       AADp=0.
       AADrou=0.
       do 55 i=1,N
       AADp=AADp+abs(errorp(i))
       AADrou=AADrou+abs(errorl(i))
55     errp=errp+errorp(i)**2.
       errl=errl+errorl(i)**2.
       AADp=AADp/N
       AADrou=AADrou/N
       rms=sqrt(errp/N+errl/N)
       write(*,*) ' C1      C2      a1      a2      b1/lmol-1  AADP(%)
      $AADL(%)'
       write(*,56) C1,C2,aa1,aa2,b,AADp,AADrou
       write(17,*) ' C1      C2      a1      a2      b1/lmol-1
       AADP(%)
      $AADL(%)'
       write(17,56) C1,C2,aa1,aa2,b,AADp,AADrou
51     format(1x,f6.2,1x,f9.6,2x,f9.6,1x,f6.2,3x,f7.2,2x,f7.2,1x,f6.2)
56     format(1x,f5.0,1x,f8.4,1x,f7.4,1x,f8.5,2x,f8.5,2x,f6.2,5x,f6.2)
       end

       SUBROUTINE NEWRAP(AVL,BVL,KK,PP,xx,sym)
       IMPLICIT REAL*8(A-H,K,N,O-Z)
       integer maxi,i,sym
       F(xx)=1-2.*(KK*PP/(xx-B)-1.)/(4.*KK*PP/(xx-B)-1.
      $-sqrt(1.+8.*KK*PP/(xx-B)))/(xx-B)+A/(xx**2.+2.*B*xx-B**2.)
       DER(xx)=2.*(KK*PP/(xx-B)-1.)/(4.*KK*PP/(xx-B)-1.
      $-sqrt(1.+8.*KK*PP/(xx-B)))/(xx-B)**2.
      $-2.*A*(xx+B)/(xx**2.+2.*B*xx-B**2.)**2.
      $ +KK*PP/(xx-B)**2.*(6.-2.*sqrt(1.+8.*KK*PP/(xx-B))
      $ +8.*(KK*PP/(xx-B)-1.)/sqrt(1.+8.*KK*PP/(xx-B)))
      $ /(4.*KK*PP/(xx-B)-1.-sqrt(1.+8.*KK*PP/(xx-B)))**2./(xx-B)
       IF (sym.EQ.1) THEN
       xini=1.001*BVL
       ELSEif (sym.eq.2) then
       xini=0.9
       ENDIF
       es=1.e-8
       maxi=1.e+7
       err = 100.
       i = 1
10     if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
         xxnew = xini - (F(xini)/DER(xini))
         if (xxnew.ne.0.) then
           err = abs((xxnew - xini)/xxnew) * 100.
         endif
         xini = xxnew
         i = i + 1
         go to 10
```

```
20     continue
       if((err.lt.es).and.(DER(xini).ne.0.)) then
       xx=xini
       elseif((err.gt.es).and.(DER(xini).ne.0.)) then
       write(*,*) 'The root is not reached within the error limit after
      $ prescribed number of iteration.'
       write(*,*)
       write(*,*) 'The approximate root =',xini
       write(*,*)
       write(*,*) 'The percentage relative error =',err
       elseif(DER(xini).eq.0.) then
       write(*,*) 'Newton''s method fails....Derivative equal to zero.'
       endif
       return
       end
```

B2. VLE Calculations from the Three Models

Model PPR-2:

```
C      This program allows you to perform the bubble-point pressure
C      calculations using Model PPR-2
C      Component 1 is associating substance, Component 2 is non-
C      associating substance
       IMPLICIT REAL*8(A-H,K,O-Z)
       INTEGER I,N
       DIMENSION Pcal(50),y1cal(50),Pexp(50),y1(50),y2(50),x1(50),x2(50)
       DIMENSION A(2),B(2),C(2),D(2),E(2)
       COMMON/SW/x1,x2
       COMMON/R1/R
       COMMON/COEF/A,B,C,D,E
       COMMON/PARAME/a11,a12,b1,H1,C1,a21,a22,b2
       COMMON/INTERPAR/k12
       OPEN(11,FILE='INPUT.TXT',STATUS='OLD')
       OPEN(16,FILE='OUTPUT.TXT',STATUS='OLD')
       READ(11,*) 'Please enter the coefficients of vapor pressure
      $      expression'
       READ(11,*) (A(i),B(i),C(i),D(i),E(i),i=1,2)
       READ(11,*) 'Please enter the coefficients of parameter for
      $      associating species'
       READ(11,*) a11,a12,b1,H1,C1
       READ(11,*) 'Please enter the coefficients of parameter for non-
      $      associating species'
       READ(11,*) a21,a22,b2
       READ(11,*) 'Please enter the binary interaction parameter'
       READ(11,*) k12
       READ(11,*) 'Number of experimental data', N
       READ(11,*) 'System temperature', tt, 'deg.C'
       READ(11,*) 'Experimental P(mmHg), x1,y1', (Pexp(i),x1(i),y1(i),
      $      I=1,N)
       R=0.0831439
       T=tt+273.15
       DO 2 i=1,N
       Pexp(i)=Pexp(i)/760.*1.01325
       y2(i)=1.-y1(i)
2      x2(i)=1.-x1(i)
```

```
      WRITE(16,*) '  xexp   pexp   pcal    errp    yexp   ycal   erry'
      CALL VBP(N,T,y1,Pexp,y1cal,Pcal)
      STOP
      END

C     This program is used to calculate the initial pressure
      SUBROUTINE VAPP(T,P)
      IMPLICIT REAL*8(A-H,K,O-Z)
      INTEGER I,J,L,m,N
      DIMENSION A(2),B(2),C(2),D(2),E(2),P(2)
      COMMON/COEF/A,B,C,D,E
      DO 111 i=1,2
111   P(i)=exp(A(i)+B(i)/T+C(i)*Log(T)+D(i)*T**E(i))/10.**5
      RETURN
      END

C     This program is used to calculate parameters for the pure
C     substances
      SUBROUTINE PARA(T,a1,a2,b1,b2,K)
      IMPLICIT REAL*8(A-H,K,O-Z)
      INTEGER I,J,L,m,N
      COMMON/PARAME/a11,a12,b1,H1,C1,a21,a22,b2
      K=exp(H1/T+C1)
      a1=(a11+a12*sqrt(T))**2.
      b1=b1/100.
      a2=(a21+a22*sqrt(T))**2.
      b2=b2/100.
      RETURN
      END

C     This program is to calculate the bubble-point pressure and vapor
C     mole fractions
      SUBROUTINE VBP(N,T,y1,Pexp,y1cal,Pin)
      IMPLICIT REAL*8(A-H,K,O-Z)
      INTEGER I,J,L,m,N
      REAL nt0v(50),nt0L(50)
      DIMENSION Pin(50),P(2),philm(50),phil2(50),phild(50)
      DIMENSION phivm(50),phiv2(50),phivd(50)
      DIMENSION zlm(50),zvm(50),zvd(50),zld(50),zl2(50),zv2(50)
      DIMENSION x1(50),x2(50),y1cal(50),y2cal(50)
      DIMENSION aal(50),bbl(50),aav(50),bbv(50)
      DIMENSION AL(50),BL(50),ZL(50),vl(50),gl(50)
      DIMENSION flm1(50),flm2(50),flm3(50),flm4(50),flm5(50),flm6(50)
      DIMENSION fl21(50),fl22(50),fl23(50),fl24(50),fl25(50),fl26(50)
      DIMENSION fld1(50),fld2(50),fld3(50),fld4(50),fld5(50),fld6(50)
      DIMENSION AV(50),BV(50),ZV(50),vv(50),gv(50)
      DIMENSION fvm1(50),fvm2(50),fvm3(50),fvm4(50),fvm5(50),fvm6(50)
      DIMENSION fv21(50),fv22(50),fv23(50),fv24(50),fv25(50),fv26(50)
      DIMENSION fvd1(50),fvd2(50),fvd3(50),fvd4(50),fvd5(50),fvd6(50)
      DIMENSION Pexp(50),y1(50),errp(50),erry(50)
      COMMON/PARAME/a11,a12,b1,H1,C1,a21,a22,b2
      COMMON/SW/x1,x2
      COMMON/R1/R
      COMMON/INTERPAR/k12
      eps=0.0001
      CALL VAPP(T,P)
      CALL PARA(T,a1,a2,b1,b2,K)
```

```
      Do 4 i=1,N
      Pin(i)=P(1)*x1(i)+P(2)*x2(i)
      y1cal(i)=x1(i)*P(1)/Pin(i)
      y2cal(i)=x2(i)*P(2)/Pin(i)
      aal(i)=x1(i)**2.*a1+2.*x1(i)*x2(i)*sqrt(a1*a2)*(1.-k12)
     $       +x2(i)**2.*a2
      bbl(i)=x1(i)*b1+x2(i)*b2
6     BL(i)=bbl(i)*Pin(i)/R/T
      AL(i)=aal(i)*Pin(i)/(R*T)**2.0
      AA=AL(i)
      BB=BL(i)
      xx1=x1(i)
      xx2=x2(i)
      KK=K
      PP=Pin(i)
      CALL NEWRAP(AA,BB,xx1,xx2,KK,PP,Z,1)
      ZL(i)=Z
      vl(i)=ZL(i)*R*T/Pin(i)
      gl(i)=((ZL(i)+(1.+sqrt(2.))*BL(i))/(ZL(i)+(1.-sqrt(2.))*BL(i)))
     $       **(AL(i)/BL(i)/2./sqrt(2.))
      nt0l(i)=x2(i)+2.0*x1(i)*(x1(i)*K*R*T/(vl(i)-bbl(i))/gl(i)-1.)
     $       /(4.*K*x1(i)*R*T/gl(i)/(vl(i)-bbl(i))-1.
     $       -sqrt(1.+8.*K*x1(i)*R*T/gl(i)/(vl(i)-bbl(i))))
      flm1(i)=-log(1.-bbl(i)/vl(i))
      flm2(i)=nt0l(i)*b1/(vl(i)-bbl(i))
      flm3(i)=-aal(i)*b1*nt0l(i)/2./sqrt(2.)/bbl(i)/bbl(i)/R/T
     $       *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $       /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      flm4(i)=((2.*x1(i)*nt0l(i)+x1(i)*x1(i)-x1(i)*x1(i)*nt0l(i))*a1
     $       +2.*sqrt(a1*a2)*(1.-k12)*x2(i)*(nt0l(i)*x2(i)+x1(i))
     $       +(1.-nt0l(i))*x2(i)*x2(i)*a2)/2./sqrt(2.)/bbl(i)/R/T
     $       *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $       /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      flm5(i)=-aal(i)*b1*vl(i)*nt0l(i)/bbl(i)/R/T
     $       /(vl(i)**2.0+2.0*bbl(i)*vl(i)-bbl(i)**2.0)
      flm6(i)=-log(Pin(i)*vl(i)/nt0l(i)/R/T)
      philm(i)=exp(flm1(i)+flm2(i)+flm3(i)+flm4(i)+flm5(i)+flm6(i))
      fld1(i)=-log(1.-bbl(i)/vl(i))
      fld2(i)=2.*nt0l(i)*b1/(vl(i)-bbl(i))
      fld3(i)=-aal(i)*b1*nt0l(i)/sqrt(2.)/bbl(i)/bbl(i)/R/T
     $       *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $       /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fld4(i)=((4.*x1(i)*nt0l(i)+x1(i)*x1(i)-2.*x1(i)*x1(i)*nt0l(i))*a1
     $       +2.*sqrt(a1*a2)*(1.-k12)*x2(i)*(2.*nt0l(i)*x2(i)+x1(i))
     $       +(1.-2.*nt0l(i))*x2(i)*x2(i)*a2)/2./sqrt(2.)/bbl(i)/R/T
     $       *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $       /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fld5(i)=-2.*aal(i)*b1*vl(i)*nt0l(i)/bbl(i)/R/T/(vl(i)**2.0+2.0
     $       *bbl(i)*vl(i)-bbl(i)**2.0)
      fld6(i)=-log(Pin(i)*vl(i)/nt0l(i)/R/T)
      phild(i)=exp(fld1(i)+fld2(i)+fld3(i)+fld4(i)+fld5(i)+fld6(i))
      fl21(i)=-log(1.-bbl(i)/vl(i))
      fl22(i)=nt0l(i)*b2/(vl(i)-bbl(i))
      fl23(i)=-aal(i)*b2*nt0l(i)/2./sqrt(2.)/bbl(i)/bbl(i)/R/T
     $       *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $       /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fl24(i)=((2.*x2(i)*nt0l(i)+x2(i)*x2(i)-x2(i)*x2(i)*nt0l(i))*a2
```

```
     $      +2.*sqrt(a1*a2)*(1.-k12)*x1(i)*(nt01(i)*x1(i)+x2(i))
     $      +(1.-nt01(i))*x1(i)*x1(i)*a1)/2./sqrt(2.)/bb1(i)/R/T
     $      *log((v1(i)+bb1(i)-sqrt(2.)*bb1(i))
     $      /(v1(i)+bb1(i)+sqrt(2.)*bb1(i)))
      fl25(i)=-aa1(i)*b2*v1(i)*nt01(i)/bb1(i)/R/T
     $      /(v1(i)**2.0+2.0*bb1(i)*v1(i)-bb1(i)**2.0)
      fl26(i)=-log(Pin(i)*v1(i)/nt01(i)/R/T)
      phi12(i)=exp(fl21(i)+fl22(i)+fl23(i)+fl24(i)+fl25(i)+fl26(i))
      z12(i)=x2(i)/nt01(i)
      zlm(i)=2.-(2.+x1(i)/x2(i))*z12(i)
      zld(i)=zlm(i)**2.*Pin(i)*K*philm(i)**2./phild(i)
      sumy1=1.
1     sumy=0.
      aav(i)=y1cal(i)**2.0*a1+2.0*y1cal(i)*y2cal(i)*sqrt(a1*a2)
     $      *(1.-k12)+y2cal(i)**2.0*a2
      bbv(i)=y1cal(i)*b1+y2cal(i)*b2
      BV(i)=bbv(i)*Pin(i)/R/T
      AV(i)=aav(i)*Pin(i)/(R*T)**2.0
      AA=AV(i)
      BB=BV(i)
      xx1=y1cal(i)
      xx2=y2cal(i)
      KK=K
      PP=Pin(i)
      CALL NEWRAP(AA,BB,xx1,xx2,KK,PP,Z,2)
      ZV(i)=Z
      vv(i)=ZV(i)*R*T/Pin(i)
      gv(i)=((ZV(i)+(1.+sqrt(2.))*BV(i))/(ZV(i)+(1.-sqrt(2.))*BV(i)))
     $      **(AV(i)/BV(i)/2./sqrt(2.))
      nt0v(i)=y2cal(i)+2.0*y1cal(i)*(y1cal(i)*K*R*T/(vv(i)-
     $      bbv(i))/gv(i)-1.)/(4.*K*y1cal(i)*R*T/gv(i)/(vv(i)-bbv(i))
     $      -1.-sqrt(1.+8.*K*y1cal(i)*R*T/gv(i)/(vv(i)-bbv(i))))
      fvm1(i)=-log(1.-bbv(i)/vv(i))
      fvm2(i)=nt0v(i)*b1/(vv(i)-bbv(i))
      fvm3(i)=-aav(i)*b1*nt0v(i)/2./sqrt(2.)/bbv(i)/bbv(i)/R/T
     $      *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $      /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvm4(i)=((2.*y1cal(i)*nt0v(i)+y1cal(i)*y1cal(i)-y1cal(i)*y1cal(i)
     $*nt0v(i))*a1+2.*sqrt(a1*a2)*(1.-k12)*y2cal(i)*(nt0v(i)*y2cal(i)
     $+y1cal(i))+(1.-nt0v(i))*y2cal(i)*y2cal(i)*a2)/2./sqrt(2.)/bbv(i)
     $/R/T*log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $/(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvm5(i)=-aav(i)*b1*vv(i)*nt0v(i)/bbv(i)/R/T
     $      /(vv(i)**2.0+2.0*bbv(i)*vv(i)-bbv(i)**2.0)
      fvm6(i)=-log(Pin(i)*vv(i)/nt0v(i)/R/T)
      phivm(i)=exp(fvm1(i)+fvm2(i)+fvm3(i)+fvm4(i)+fvm5(i)+fvm6(i))
      fvd1(i)=-log(1.-bbv(i)/vv(i))
      fvd2(i)=2.*nt0v(i)*b1/(vv(i)-bbv(i))
      fvd3(i)=-aav(i)*b1*nt0v(i)/sqrt(2.)/bbv(i)/bbv(i)/R/T
     $      *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $      /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
     $      fvd4(i)=((4.*y1cal(i)*nt0v(i)+y1cal(i)*y1cal(i)
     $      -2.*y1cal(i)*y1cal(i)*nt0v(i))*a1
     $+2.*sqrt(a1*a2)*(1.-k12)*y2cal(i)*(2.*nt0v(i)*y2cal(i)+y1cal(i))
     $+(1.-2.*nt0v(i))*y2cal(i)*y2cal(i)*a2)/2./sqrt(2.)/bbv(i)/R/T
     $      *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $      /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
```

```
      fvd5(i)=-2.*aav(i)*b1*vv(i)*nt0v(i)/bbv(i)/R/T/(vv(i)**2.0+2.0
     $      *bbv(i)*vv(i)-bbv(i)**2.0)
      fvd6(i)=-log(Pin(i)*vv(i)/nt0v(i)/R/T)
      phivd(i)=exp(fvd1(i)+fvd2(i)+fvd3(i)+fvd4(i)+fvd5(i)+fvd6(i))
      fv21(i)=-log(1.-bbv(i)/vv(i))
      fv22(i)=nt0v(i)*b2/(vv(i)-bbv(i))
      fv23(i)=-aav(i)*b2*nt0v(i)/2./sqrt(2.)/bbv(i)/bbv(i)/R/T
     $      *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $      /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fv24(i)=((2.*y2cal(i)*nt0v(i)+y2cal(i)*y2cal(i)-y2cal(i)*y2cal(i)
     $*nt0v(i))*a2+2.*sqrt(a1*a2)*(1.-k12)*y1cal(i)*(nt0v(i)*y1cal(i)
     $+y2cal(i))+(1.-nt0v(i))*y1cal(i)*y1cal(i)*a1)/2./sqrt(2.)/bbv(i)
     $      /R/T*log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $      /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fv25(i)=-aav(i)*b2*vv(i)*nt0v(i)/bbv(i)/R/T
     $      /(vv(i)**2.0+2.0*bbv(i)*vv(i)-bbv(i)**2.0)
      fv26(i)=-log(Pin(i)*vv(i)/nt0v(i)/R/T)
      phiv2(i)=exp(fv21(i)+fv22(i)+fv23(i)+fv24(i)+fv25(i)+fv26(i))
      zv2(i)=phil2(i)*zl2(i)/phiv2(i)
      zvm(i)=philm(i)*zlm(i)/phivm(i)
      zvd(i)=phild(i)*zld(i)/phivd(i)
      sumy=sumy+zv2(i)+zvm(i)+zvd(i)
      IF (abs(sumy-sumy1).LE.eps) goto 16
      zv2(i)=zv2(i)/sumy
      zvm(i)=zvm(i)/sumy
      zvd(i)=zvd(i)/sumy
      y1cal(i)=(zvm(i)+2.*zvd(i))/(zvm(i)+2.*zvd(i)+zv2(i))
      y2cal(i)=1.-y1cal(i)
      sumy1=sumy
      GOTO 1
16    sy=sumy-1.0
      IF (abs(sy).GT.eps) THEN
      Pin(i)=Pin(i)*(2.-1./(zv2(i)+zvm(i)+zvd(i)))
      GOTO 6
      ENDIF
      errp(i)=(Pin(i)-Pexp(i))/Pexp(i)*100.
      erry(i)=y1cal(i)-y1(i)
      WRITE(16,123) x1(i),Pexp(i),Pin(i),errp(i),y1(i),y1cal(i),erry(i)
4     CONTINUE
      AADY=0.0
      AADP=0.0
      Do 8 j=1,N
      AADY=AADY+ABS(y1cal(j)-y1(j))
8     AADP=AADP+ABS((Pin(j)-Pexp(j))/Pexp(j))
      OF=AADY/N+AADP/N
      WRITE(16,92) T-273.15,k12,AADP/N,AADY/N,OF
92    FORMAT(1x,f6.2,1x,f6.4,2x,f6.4,2x,f6.4,2x,f7.3)
121   FORMAT(1x,f6.4,1x,f6.4,1x,f6.4)
122   FORMAT(1x,f6.4,1x,f6.4,1x,f6.4,1x,f8.4,1x,f6.4,1x,f6.4,1x,f6.4)
123   FORMAT(1x,f6.4,1x,f6.4,1x,f6.4,1x,f8.4,1x,f6.4,1x,f6.4,1x,f6.4)
      RETURN
      END

C     This program is used to solve the roots of EOS
      SUBROUTINE NEWRAP(A,B,xx1,xx2,KK,PP,xx,sym)
      REAL KK
      INTEGER I,sym
```

```
C     Defining the Function 'F(xx)=0' to be solved
      F(xx)=(xx2+2.*xx1*(xx1*KK*PP/((xx+(1+sqrt(2.))*B)
     $       /(xx+(1-sqrt(2.))*B))**(A/B/2./sqrt(2.))/(xx-B)-1.)
     $       /(4.*KK*PP*xx1/((xx+(1+sqrt(2.))*B)/(xx+(1-sqrt(2.))*B))
     $       **(A/B/2./sqrt(2.))/(xx-B)-1.-sqrt(1.+8.*KK*PP*xx1
     $/((xx+(1+sqrt(2.))*B)/(xx+(1-sqrt(2.))*B))**(A/B/2./sqrt(2.))
     $       /(xx-B))))*(1./(xx-B)-A/(xx**2.0+2.0*B*xx-B**2.0))-1.
C     Defining the Function for derivative of 'F(xx)'
      DER(xx)=(xx2+2.*xx1*((KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)
     $/(xx+(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.)))-1.)/(4.*(KK*xx1*PP
     $/(xx-B)/((xx+(1.+sqrt(2.))*B)/(xx+(1.-sqrt(2.))*B))**(A/B/2.
     $/sqrt(2.)))-1.-sqrt(1.+8.*(KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)
     $/(xx+(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.))))))
     $*(-1./(xx-B)**2.-2.*A*(xx+B)/(xx**2.+2.*B*xx-B**2.)**2.)
     $+2.*xx1*(KK*xx1*PP*(A*(xx-B)/(xx+(1.-sqrt(2.))*B)/(xx
     $+(1.+sqrt(2.))*B)-1.)/(xx-B)**2.
     $/((xx+(1.+sqrt(2.))*B)/(xx+(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.)))
     $*(4.*(KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)/(xx+
     $(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.)))-1.-sqrt(1.+8.*(KK*xx1*PP
     $/(xx-B)/((xx+(1.+sqrt(2.))*B)/(xx+(1.-sqrt(2.))*B))
     $**(A/B/2./sqrt(2.))))-4.*((KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)
     $/(xx+(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.)))-1.)*(1.-1./sqrt(1.+8.
     $*(KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)/(xx+(1.-sqrt(2.))*B))
     $**(A/B/2./sqrt(2.))))))
     $/(4.*(KK*xx1*PP/(xx-B)/((xx+(1.+sqrt(2.))*B)/(xx+(1.-
     $sqrt(2.))*B))**(A/B/2./sqrt(2.)))-1.-sqrt(8.*(KK*xx1*PP/(xx-B)
     $/((xx+(1.+sqrt(2.))*B)/(xx+(1.-sqrt(2.))*B))**(A/B/2./sqrt(2.)))
     $+1.))**2.*(1./(xx-B)-A/(xx**2.+2.*B*xx-B**2))
      IF (sym.EQ.1) THEN
      xini=1.0001*B
      ELSE
      xini=0.9
      ENDIF
      es=1.e-8
      maxi=1.e+7
      err = 100.
      i = 1
10    IF((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) goto 20
      xxnew = xini - (F(xini)/DER(xini))
      IF (xxnew.ne.0.) THEN
      err = abs((xxnew - xini)/xxnew) * 100.
      ENDIF
      xini = xxnew
      i = i + 1
      goto 10
20    CONTINUE
      IF((err.lt.es).and.(DER(xini).le.0.)) THEN
      WRITE(16,*) 'The root within the prescribed error Limit is:',xini
      WRITE(16,*)
      WRITE(16,*)'The number of iteration performed before achieving'
      WRITE(16,*)'acceptable error Limit is:',i - 1
      xx=xini
      ELSEIF((err.gt.es).and.(DER(xini).ne.0.)) THEN
      WRITE(*,*) 'The root is not reached within the error Limit after
     $      prescribed number of iteration.'
      WRITE(*,*) 'The approximate root =',xini
      WRITE(*,*) 'The percentage relative error =',err
```

```
      ELSEIF(DER(xini).eq.0.) THEN
      WRITE(*,*) 'Newton's method fails....Derivative equal to zero.'
      ENDIF
      RETURN
      END
```

Model PPR-3:

```
C     This program allows you to perform the bubble-point pressure
C     calculations using Model PPR-3
C     Component 1 is nonassociating substance, Component 2 is
C     associating substance
C     test hydrocarnon(1)-alcohol(2) system
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,N)
      DIMENSION Pcal(50),y1cal(50),Pexp(50),y1(50)
      DIMENSION x1(50),x2(50),y2(50),w(2)
      DIMENSION A(2),B(2),C(2),D(2),E(2)
      COMMON/R1/R
      COMMON/WW/w
      COMMON/COEF/A,B,C,D,E
      COMMON/SW/x1,x2
      COMMON/PARAME/a11,a12,b11,a21,a22,a23,b21,b22,H1,H2
      COMMON/INTERPAR/k12
      OPEN(11,FILE='input.txt',STATUS='old')
      OPEN(17,file='output.txt',status='old')
      READ(11,*) (A(i),B(i),C(i),D(i),E(i),i=1,2)
      READ(11,*) a11,a12
      READ(11,*) b11
      READ(11,*) a21,a22,a23
      READ(11,*) b21,b22
      READ(11,*) H1,H2
      Read(11,*) N,tt,k12
      READ(11,*) (Pexp(I),x1(I),y1(I), I=1,N)
      R=0.0831439
      T=tt+273.15
      write(*,*) ' x1exp    pexp   pcaL    errp    y1exp   y1caL  erry'
      write(17,*) ' x1exp    pexp   pcaL    errp    y1exp   ycaL  erry'
      Do 2 i=1,N
      Pexp(i)=Pexp(i)/760.*1.01325
      y2(i)=1-y1(i)
2     x2(i)=1-x1(i)
      CALL vbp(N,T,y1,Pexp,y1cal,Pcal)
      end

      SUBROUTINE vapp(T,P)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      DIMENSION A(2),B(2),C(2),D(2),E(2),P(2)
      COMMON/COEF/A,B,C,D,E
      Do 111 i=1,2
111   P(i)=exp(A(i)+B(i)/T+C(i)*log(T)+D(i)*T**E(i))/10.**5
      RETURN
      END

      SUBROUTINE para(T,a1,a2,b1,b2,K)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      COMMON/PARAME/a11,a12,b11,a21,a22,a23,b21,b22,H1,H2
      K=exp(H1/T+H2)
```

```
      a2=a21+a22*sqrt(T)+a23*T
      b2=(b21+b22*sqrt(T))**2.
      a1=(a11+a12*sqrt(T))**2.
      b1=b11/100.
      RETURN
      END

      SUBROUTINE vbp(N,T,y1,Pexp,y1cal,Pin)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      REAL nt0v(50),nt0l(50)
      DIMENSION Pin(50),x1(50),x2(50),y1cal(50),y2cal(50),P(2)
      DIMENSION aal(50),bbl(50),aav(50),bbv(50),y2(50)
      DIMENSION BL(50),AL(50),BV(50),AV(50)
      DIMENSION ZL(50),ZV(50),vl(50),vv(50)
      DIMENSION qq1(2,50),qq2(2,50),qq3(2,50),qq4(2,50),qq5(2,50)
      DIMENSION ww1(2,50),ww2(2,50),ww3(2,50),ww4(2,50),ww5(2,50)
      DIMENSION phiv(2,50),phil(2,50),Pexp(50),y1(50),w(2)
      DIMENSION z1V(50),z1L(50),z2V(50),z2L(50),errorp(50),errory(50)
      COMMON/SW/x1,x2
      COMMON/R1/R
      COMMON/WW/w
      COMMON/INTERPAR/k12
      eps=0.0001
      k12=-0.069
      CALL vapp(T,P)
      CALL para(T,a1,a2,b1,b2,K)
      Do 4 i=1,N
      Pin(i)=P(1)*x1(i)+P(2)*x2(i)
      y1cal(i)=P(1)/Pin(i)*x1(i)
      y2cal(i)=P(2)/Pin(i)*x2(i)
      aal(i)=x1(i)**2.0*a1+2.0*x1(i)*x2(i)*sqrt(a1*a2)*(1.-k12)
     $        +x2(i)**2.0*a2
      bbl(i)=x1(i)*b1+x2(i)*b2
7     BL(i)=bbl(i)*Pin(i)/R/T
      AL(i)=aal(i)*Pin(i)/(R*T)**2.0
      CALL NEWRAP(AL(i),BL(i),x1(i),x2(i),K,Pin(i),ZL(i),1)
      vl(i)=ZL(i)*R*T/Pin(i)
      nt0l(i)=x1(i)+2.0*x2(i)/(1.+sqrt(1.+4.*K*R*T*x2(i)
     $      /(vl(i)-bbl(i))))
      ww1(1,i)=-log(1.-bbl(i)/vl(i))
      ww2(1,i)=nt0l(i)*b1/(vl(i)-bbl(i))
      ww3(1,i)=-aal(i)*b1*vl(i)/bbl(i)/R/T/(vl(i)**2.0+2.0*bbl(i)
     $      *vl(i)-bbl(i)**2.0)
      ww4(1,i)=(2.*(x1(i)*a1+x2(i)*sqrt(a1*a2)*(1.-k12))-aal(i)*b1
     $      /bbl(i))/2./sqrt(2.)/bbl(i)/R/T*log((vl(i)+bbl(i)-sqrt(2.)
     $      *bbl(i))/(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      ww5(1,i)=-log(Pin(i)*vl(i)/nt0l(i)/R/T)
      phil(1,i)=exp(ww1(1,i)+ww2(1,i)+ww3(1,i)+ww4(1,i)+ww5(1,i))
      ww1(2,i)=ww1(1,i)
      ww2(2,i)=nt0l(i)*b2/(vl(i)-bbl(i))
      ww3(2,i)=-aal(i)*b2*vl(i)/bbl(i)/R/T/(vl(i)**2.0+2.0*bbl(i)
     $      *vl(i)-bbl(i)**2.0)
      ww4(2,i)=(2.*(x1(i)*sqrt(a1*a2)*(1.-k12)+x2(i)*a2)-aal(i)*b2
     $      /bbl(i))/2./sqrt(2.)/bbl(i)/R/T*log((vl(i)+bbl(i)-sqrt(2.)
     $      *bbl(i))/(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      ww5(2,i)=ww5(1,i)
      phil(2,i)=exp(ww1(2,i)+ww2(2,i)+ww3(2,i)+ww4(2,i)+ww5(2,i))
```

```
      z1L(i)=x1(i)/nt0l(i)
      z2L(i)=(x1(i)/nt0l(i)-1.0)/(K*R*T*x1(i)/(vl(i)-bbl(i))-K*R*T
     $      /(vl(i)-bbl(i))*nt0l(i)-1.0)
      sumy1=1.0
5     sumy=0.0
      aav(i)=y1cal(i)**2.0*a1+2.0*y1cal(i)*y2cal(i)*sqrt(a1*a2)
     $      *(1.-k12)+y2cal(i)**2.0*a2
      bbv(i)=y1cal(i)*b1+y2cal(i)*b2
      BV(i)=bbv(i)*Pin(i)/R/T
      AV(i)=aav(i)*Pin(i)/(R*T)**2.0
      CALL NEWRAP(AV(i),BV(i),y1cal(i),y2cal(i),K,Pin(i),ZV(i),2)
      vv(i)=ZV(i)*R*T/Pin(i)
      nt0v(i)=y1cal(i)+2.0*y2cal(i)/(1.+sqrt(1.+4.0*K*R*T*y2cal(i)
     $            /(vv(i)-bbv(i))))
      qq1(1,i)=-log(1.-bbv(i)/vv(i))
      qq2(1,i)=nt0v(i)*b1/(vv(i)-bbv(i))
      qq3(1,i)=-aav(i)*b1*vv(i)/bbv(i)/R/T/(vv(i)**2.0+2.0*bbv(i)
     $      *vv(i)-bbv(i)**2.0)
      qq4(1,i)=(2.*(y1cal(i)*a1+y2cal(i)*sqrt(a1*a2)*(1.-k12))-
     $aav(i)*b1/bbv(i))/2./sqrt(2.)/bbv(i)/R/T*log((vv(i)+bbv(i)-
     $ sqrt(2.)*bbv(i))/(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      qq5(1,i)=-log(Pin(i)*vv(i)/nt0v(i)/R/T)
      phiv(1,i)=exp(qq1(1,i)+qq2(1,i)+qq3(1,i)+qq4(1,i)+qq5(1,i))
      qq1(2,i)=qq1(1,i)
      qq2(2,i)=nt0v(i)*b2/(vv(i)-bbv(i))
      qq3(2,i)=-aav(i)*b2*vv(i)/bbv(i)/R/T/(vv(i)**2.0+2.0*bbv(i)
     $      *vv(i)-bbv(i)**2.0)
      qq4(2,i)=(2.*(y1cal(i)*sqrt(a1*a2)*(1.-k12)+y2cal(i)*a2)-av(i)*b2
     $      /bbv(i))/2./sqrt(2.)/bbv(i)/R/T*log((vv(i)+bbv(i)-sqrt(2.)
     $      *bbv(i))/(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      qq5(2,i)=qq5(1,i)
      phiv(2,i)=exp(qq1(2,i)+qq2(2,i)+qq3(2,i)+qq4(2,i)+qq5(2,i))
      z1V(i)=z1L(i)*phil(1,i)/phiv(1,i)
      y1cal(i)=z1V(i)*nt0v(i)
      z2V(i)=z2L(i)*phil(2,i)/phiv(2,i)
      y2cal(i)=z2V(i)*nt0v(i)/(1-K*nt0v(i)*R*T/(vv(i)-bv(i))*z2V(i))**2
      sumy=sumy+y1cal(i)+y2cal(i)
      if (abs(sumy-sumy1).LE.eps) goto 6
      y1cal(i)=y1cal(i)/sumy
      y2cal(i)=y2cal(i)/sumy
      sumy1=sumy
      goto 5
6     sy=sumy-1.0
      IF (abs(sy).GT.eps) then
      Pin(i)=Pin(i)*(2.-1./(y1cal(i)+y2cal(i)))
      GOTO 7
      ENDIF
      y2(i)=1.-y1(i)
141   errorp(i)=(Pin(i)-pexp(i))/pexp(i)*100.
      errory(i)=y2cal(i)-y2(i)
      write(*,9)x2(i),pexp(i),Pin(i),errorp(i),y2(i),y2cal(i),errory(i)
      write(17,9)x2(i),pexp(i),Pin(i),errorp(i),y2(i),y2cal(i),
     $      errory(i)
9     format(1x,f6.4,2x,f6.4,2x,f6.4,2x,f7.3,1x,f6.4,1x,f6.4,1x,f6.4)
4     CONTINUE
      AADY=0.0
      AADP=0.0
```

```
      DP=0.
      Do 8 j=1,N
      AADY=AADY+ABS(y1caL(j)-y1(j))
      DP=DP+abs(Pin(j)-Pexp(j))
8     AADP=AADP+ABS((Pin(j)-Pexp(j))/Pexp(j))
      OF=AADY/N+AADP/N
      write(*,*)'t/C     k12    AADP/N    AADY/N    OF  deltaP/Kpa'
      write(*,92) T-273.15,k12,AADP/N,AADY/N,OF,DP/N*100.
      write(17,*)'t/C     k12    AADP/N    AADY/N    OF  deltaP/Kpa'
      write(17,92) T-273.15,k12,AADP/N,AADY/N,OF,DP/N*100.
92    format(1x,f6.2,1x,f6.4,2x,f6.4,2x,f6.4,2x,f7.3,1x,f7.4)
      RETURN
      END

      SUBROUTINE NEWRAP(A,B,xx1,xx2,KK,PP,xx,sym)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      integer sym
      F(xx)=1.-(xx1+2.*xx2/(1.+sqrt(1.+4.*KK*PP*xx2/(xx-B))))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
      DER(xx)=(xx1+2.*xx2/(1.+sqrt(1.+(4.*KK*PP*xx2/(xx-B)))))
     $      /(xx-B)**2.0-4.0*xx2**2.0*KK*PP/(xx-B)**3.0
     $      /(1.+sqrt(1.+4.*KK*PP*xx2/(xx-B)))**2.0
     $      /sqrt(1.+4.*KK*PP*xx2/(xx-B))-2.0*A*(xx+B)
     $      /(xx**2.0+2.*B*xx-B**2.0)**2.
      IF (sym.EQ.1) THEN
      xini=1.0001*B
      ELSE
      xini=0.9
      ENDIF
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
C     write(*,*) xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
        write(6,*) 'The root is not reached within the error limit
     $      after prescribed number of iteration.'
        write(6,*)
        write(6,*) 'The approximate root =',xini
        write(6,*)
        write(6,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
        write(6,*) 'Newton''s method fails...Derivative equal to zero.'
      endif
      return
      end
```

Model PPR-4:

```
C     This program allows you to perform the bubble-point temperature
C     calculations using Model PPR-4
C     Component 1 is associating substance, Component 2 is non-
C     associating substance
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      DIMENSION ttexp(50),Tcal(50),Texp(50),omega(2),TC(2)
      DIMENSION y1(50),y2(50),x1(50),x2(50),y1cal(50)
      DIMENSION A(2),B(2),C(2),D(2),E(2),tt(2),Try(50)
      COMMON/R1/R
      COMMON/SW/x1,x2
      COMMON/COEF/A,B,C,D,E
      COMMON/PARAME/a11,a12,a13,b11,a21,a22,b21,H1,H2
      COMMON/PHYPRO/omega,TC
      COMMON/INTERPAR/k12
      OPEN(11,FILE='input.txt',STATUS='old')
      OPEN(16,file='out.txt',status='old')
      READ(11,*) (A(i),B(i),C(i),D(i),E(i),i=1,2)
      READ(11,*) (omega(i),TC(i),i=1,2)
      READ(11,*) a11,a12,a13
      READ(11,*) b11
      READ(11,*) a21,a22
      READ(11,*) b21
      READ(11,*) H1,H2
      Read(11,*) N,Ps,k12
      READ(11,*) (ttexp(i),x2(I),y2(I), I=1,N)
      R=0.0831439
      Ps=Ps/760.*1.01325
      Do 2 i=1,N
      Texp(i)=ttexp(i)+273.15
      y1(i)=1.-y2(i)
2     x1(i)=1.-x2(i)
      Call bpt(Ps*10**5.,A(1),B(1),C(1),D(1),E(1),tt(1))
      Call bpt(Ps*10**5.,A(2),B(2),C(2),D(2),E(2),tt(2))
      Do 12 i=1,N
      Try(i)=tt(1)*x1(i)+tt(2)*x2(i)
12    continue
      write(16,*) "  x1  Texp/K  Tcal/K   err(T)  y1exp  y1cal err(y)"
      write(*,*) "  x1  Texp/C  Tcal/C   err(T)  y1exp  y1cal err(y)"
      CALL vbp(N,Ps,Texp,Try,Tcal,y1,y1cal)
      end

      SUBROUTINE bpt(P,aa,bb,cc,dd,ee,xx)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      error=0.03
      step=0.1
      xx=273.15
222   xx=xx+step
      F=(exp(aa+bb/xx+cc*log(xx)+dd*xx**ee)-P)/10.**5
      if (abs(F).le.error) goto 221
      goto 222
221   write(*,*)
      return
      end
```

```
      SUBROUTINE vapp(T,P)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      DIMENSION A(2),B(2),C(2),D(2),E(2),P(2)
      COMMON/COEF/A,B,C,D,E
      Do 111 i=1,2
111   P(i)=exp(A(i)+B(i)/T+C(i)*log(T)+D(i)*T**E(i))/10.**5
      RETURN
      END

      SUBROUTINE para(T,a1,a2,b1,b2,K)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      COMMON/PARAME/a11,a12,a13,b11,a21,a22,b21,H1,H2
      K=exp(H1/T+H2)
      a1=a11+a12*sqrt(T)+a13*T
      b1=b11
      a2=(a21+a22*sqrt(T))**2.
      b2=b21/100.
      RETURN
      END

      SUBROUTINE  vbp(N,Ps,Texp,Try,Tcal,y1,y1cal)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m)
      REAL nt0v(50),nt0l(50)
      DIMENSION P(2),omega(2),TC(2)
      DIMENSION Texp(50),Tcal(50),Try(50)
      DIMENSION x1(50),x2(50),y1(50),y1cal(50),y2cal(50)
      DIMENSION zl2(50),zlm(50),zld(50),zv2(50),zvm(50),zvd(50)
      DIMENSION aal(50),bbl(50),aav(50),bbv(50)
      DIMENSION AL(50),BL(50),ZL(50),vl(50)
      DIMENSION flm1(50),flm2(50),flm3(50),flm4(50),flm5(50),flm6(50)
      DIMENSION fld1(50),fld2(50),fld3(50),fld4(50),fld5(50),fld6(50)
      DIMENSION fl21(50),fl22(50),fl23(50),fl24(50),fl25(50),fl26(50)
      DIMENSION philm(50),phild(50),phil2(50)
      DIMENSION AV(50),BV(50),ZV(50),vv(50)
      DIMENSION fvm1(50),fvm2(50),fvm3(50),fvm4(50),fvm5(50),fvm6(50)
      DIMENSION fvd1(50),fvd2(50),fvd3(50),fvd4(50),fvd5(50),fvd6(50)
      DIMENSION fv21(50),fv22(50),fv23(50),fv24(50),fv25(50),fv26(50)
      DIMENSION phivm(50),phivd(50),phiv2(50)
      DIMENSION errT(50),erry(50)
      COMMON/SW/x1,x2
      COMMON/R1/R
      COMMON/PHYPRO/omega,TC
      COMMON/INTERPAR/k12
      eps=0.0005
      Do 4 i=1,N
      T=Try(i)
7     CALL vapp(T,P)
      CALL para(T,a1,a2,b1,b2,K)
      y1cal(i)=x1(i)*P(1)/Ps
      y2cal(i)=x2(i)*P(2)/Ps
      y1cal(i)=y1cal(i)/(y1cal(i)+y2cal(i))
      y2cal(i)=1.-y1cal(i)
      aal(i)=x1(i)**2.0*a1+2.0*x1(i)*x2(i)*sqrt(a1*a2)*(1.-k12)
     $          +x2(i)**2.0*a2
      bbl(i)=x1(i)*b1+x2(i)*b2
      BL(i)=bbl(i)*Ps/R/T
      AL(i)=aal(i)*Ps/(R*T)**2.0
```

```
      CALL NEWRAP(AL(i),BL(i),x1(i),x2(i),K,Ps,ZL(i),1)
      vl(i)=ZL(i)*R*T/Ps
      nt0l(i)=x2(i)+2.0*x1(i)*(x1(i)*K*R*T/(vl(i)-bbl(i))-1.)
     $ /(4.*K*x1(i)*R*T/(vl(i)-bbl(i))-1.
     $ -sqrt(1.+8.*K*x1(i)*R*T/(vl(i)-bbl(i))))
      flm1(i)=-log(1.-bbl(i)/vl(i))
      flm2(i)=nt0l(i)*b1/(vl(i)-bbl(i))
      flm3(i)=-aal(i)*b1/2./sqrt(2.)/bbl(i)/bbl(i)/R/T
     $ *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      flm4(i)=(x1(i)*a1+sqrt(a1*a2)*(1.-k12)*x2(i))/sqrt(2.)/bbl(i)/R/T
     $ *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      flm5(i)=-aal(i)*b1*vl(i)/bbl(i)/R/T/(vl(i)**2.0+2.0*bbl(i)
     $       *vl(i)-bbl(i)**2.0)
      flm6(i)=-log(Ps*vl(i)/nt0l(i)/R/T)
      philm(i)=exp(flm1(i)+flm2(i)+flm3(i)+flm4(i)+flm5(i)+flm6(i))
      fld1(i)=-log(1.-bbl(i)/vl(i))
      fld2(i)=2.*nt0l(i)*b1/(vl(i)-bbl(i))
      fld3(i)=-aal(i)*b1/sqrt(2.)/bbl(i)/bbl(i)/R/T
     $ *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fld4(i)=2.*(x1(i)*a1+sqrt(a1*a2)*(1.-12)*x2(i))/sqrt(2.)/bbl(i)/R
     $ /T*log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fld5(i)=-2.*aal(i)*b1*vl(i)/bbl(i)/R/T/(vl(i)**2.0+2.0
     $       *bbl(i)*vl(i)-bbl(i)**2.0)
      fld6(i)=-log(Ps*vl(i)/nt0l(i)/R/T)
      phild(i)=exp(fld1(i)+fld2(i)+fld3(i)+fld4(i)+fld5(i)+fld6(i))
      fl21(i)=-log(1.-bbl(i)/vl(i))
      fl22(i)=nt0l(i)*b2/(vl(i)-bbl(i))
      fl23(i)=-aal(i)*b2/2./sqrt(2.)/bbl(i)/bbl(i)/R/T
     $ *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fl24(i)=(x2(i)*a2+sqrt(a1*a2)*(1.-k12)*x1(i))/sqrt(2.)/bbl(i)/R/T
     $ *log((vl(i)+bbl(i)-sqrt(2.)*bbl(i))
     $ /(vl(i)+bbl(i)+sqrt(2.)*bbl(i)))
      fl25(i)=-aal(i)*b2*vl(i)/bbl(i)/R/T/(vl(i)**2.0+2.0*bbl(i)
     $       *vl(i)-bbl(i)**2.0)
      fl26(i)=-log(Ps*vl(i)/nt0l(i)/R/T)
      phil2(i)=exp(fl21(i)+fl22(i)+fl23(i)+fl24(i)+fl25(i)+fl26(i))
      if (x2(i).eq.0.) then
      zl2(i)=0.
      zlm(i)=(-3.+sqrt(1+8.*K*R*T/(vl(i)-bbl(i))))
     $       /2./(K*R*T/(vl(i)-bbl(i))-1.)
      zld(i)=zlm(i)**2.*Ps*K*philm(i)**2./phild(i)
      else
      zl2(i)=x2(i)/nt0l(i)
      zlm(i)=2.-(2.+x1(i)/x2(i))*zl2(i)
      zld(i)=zlm(i)**2.*Ps*K*philm(i)**2./phild(i)
      endif
      sumyl=1.
1     sumy=0.
      aav(i)=y1cal(i)**2.0*a1+2.0*y1cal(i)*y2cal(i)*sqrt(a1*a2)
     $       *(1.-k12)+y2cal(i)**2.0*a2
      bbv(i)=y1cal(i)*b1+y2cal(i)*b2
      BV(i)=bbv(i)*Ps/R/T
```

```
      AV(i)=aav(i)*Ps/(R*T)**2.0
      CALL NEWRAP(AV(i),BV(i),y1cal(i),y2cal(i),K,Ps,ZV(i),2)
      vv(i)=ZV(i)*R*T/Ps
      nt0v(i)=y2cal(i)+2.0*y1cal(i)*(y1cal(i)*K*R*T/(vv(i)-bbv(i))
     $      -1.)/(4.*K*y1cal(i)*R*T/(vv(i)-bbv(i))-1.
     $ -sqrt(1.+8.*K*y1cal(i)*R*T/(vv(i)-bbv(i))))
      fvm1(i)=-log(1.-bbv(i)/vv(i))
      fvm2(i)=nt0v(i)*b1/(vv(i)-bbv(i))
      fvm3(i)=-aav(i)*b1/2./sqrt(2.)/bbv(i)/bbv(i)/R/T
     $ *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvm4(i)=(y1cal(i)*a1+sqrt(a1*a2)*(1.-k12)*y2cal(i))
     $ /sqrt(2.)/bbv(i)/R/T*log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvm5(i)=-aav(i)*b1*vv(i)/bbv(i)/R/T/(vv(i)**2.0+2.0*bbv(i)
     $      *vv(i)-bbv(i)**2.0)
      fvm6(i)=-log(Ps*vv(i)/nt0v(i)/R/T)
      phivm(i)=exp(fvm1(i)+fvm2(i)+fvm3(i)+fvm4(i)+fvm5(i)+fvm6(i))
      fvd1(i)=-log(1.-bbv(i)/vv(i))
      fvd2(i)=2.*nt0v(i)*b1/(vv(i)-bbv(i))
      fvd3(i)=-aav(i)*b1/sqrt(2.)/bbv(i)/bbv(i)/R/T
     $ *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvd4(i)=2.*(y1cal(i)*a1+sqrt(a1*a2)*(1.-k12)*y2cal(i))/sqrt(2.)
     $ /bbv(i)/R/T*log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fvd5(i)=-2.*aav(i)*b1*vv(i)/bbv(i)/R/T/(vv(i)**2.0+2.0
     $      *bbv(i)*vv(i)-bbv(i)**2.0)
      fvd6(i)=-log(Ps*vv(i)/nt0v(i)/R/T)
      phivd(i)=exp(fvd1(i)+fvd2(i)+fvd3(i)+fvd4(i)+fvd5(i)+fvd6(i))
      fv21(i)=-log(1.-bbv(i)/vv(i))
      fv22(i)=nt0v(i)*b2/(vv(i)-bbv(i))
      fv23(i)=-aav(i)*b2/2./sqrt(2.)/bbv(i)/bbv(i)/R/T
     $ *log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fv24(i)=(y2cal(i)*a2+sqrt(a1*a2)*(1.-k12)*y1cal(i))/sqrt(2.)
     $ /bbv(i)/R/T*log((vv(i)+bbv(i)-sqrt(2.)*bbv(i))
     $ /(vv(i)+bbv(i)+sqrt(2.)*bbv(i)))
      fv25(i)=-aav(i)*b2*vv(i)/bbv(i)/R/T/(vv(i)**2.0+2.0*bbv(i)
     $      *vv(i)-bbv(i)**2.0)
      fv26(i)=-log(Ps*vv(i)/nt0v(i)/R/T)
      phiv2(i)=exp(fv21(i)+fv22(i)+fv23(i)+fv24(i)+fv25(i)+fv26(i))
      zv2(i)=phil2(i)*zl2(i)/phiv2(i)
      zvm(i)=philm(i)*zlm(i)/phivm(i)
      zvd(i)=phild(i)*zld(i)/phivd(i)
      sumy=sumy+zv2(i)+zvm(i)+zvd(i)
      if (abs(sumy-sumy1).LE.eps) goto 6
      zv2(i)=zv2(i)/sumy
      zvm(i)=zvm(i)/sumy
      zvd(i)=zvd(i)/sumy
      y1cal(i)=(zvm(i)+2.*zvd(i))/(zvm(i)+2.*zvd(i)+zv2(i))
      y2cal(i)=1.-y1cal(i)
      sumy1=sumy
      goto 1
6     sy=sumy-1.0
      IF (abs(sy).GT.eps) then
      ep=T/(5.373*((1.+omega(1))*TC(1)*(zvm(i)+zvd(i))
```

```
$      +(1.+omega(2))*TC(2)*zv2(i)))
 T=T*(1.-ep*(zv2(i)+zvm(i)+zvd(i)-1.))
 GOTO 7
 ENDIF
 y1cal(i)=(zvm(i)+2.*zvd(i))/(zvm(i)+2.*zvd(i)+zv2(i))
 y2cal(i)=1.-y1cal(i)
 Tcal(i)=T
 errT(i)=Tcal(i)-Texp(i)
 erry(i)=y1cal(i)-y1(i)
 write(16,122) x1(i),Texp(i)-273.15,Tcal(i)-273.15,errT(i),y1(i)
$      ,y1cal(i),erry(i)
 write(*,122) x1(i),Texp(i)-273.15,Tcal(i)-273.15,errT(i),y1(i)
$      ,y1cal(i),erry(i)
4     CONTINUE
 sumT=0.
 sumyy=0.
 Do 14 i=1,N
 sumyy=sumyy+abs(erry(i))
14    sumT=sumT+abs(errT(i))
 write(16,*)'   k12   sumT/N sumyy/N sumyy/N+sumT*10/N/Tcal(1)'
 write(16,123) k12,sumT/N,sumyy/N,sumyy/N+sumT*10./N/Tcal(1)
121   format(1x,f6.4,1x,f6.4,1x,f6.4,1x,f8.4,1x,f6.4,1x,f6.4)
122   format(1x,f6.4,2x,f6.2,2x,f6.2,2x,f6.2,1x,f6.4,1x,f6.4,1x,f6.4)
123   format(1x,f6.4,2x,f6.4,2x,f6.4,2x,f6.4)
 RETURN
 END

 SUBROUTINE NEWRAP(A,B,xx1,xx2,KK,PP,xx,sym)
 IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
 INTEGER sym
 F(xx)=1.-(xx2+2.*xx1*(xx1*KK*PP/(xx-B)
$ -1.)/(4.*xx1*KK*PP/(xx-B)-1.-sqrt(1.+8.*xx1*KK*PP/(xx-B))))
$ /(xx-B)+A/(xx**2.+2.*B*xx-B**2.)
 DER(xx)=(xx2+2.*xx1*(xx1*KK*PP/(xx-B)-1.)
$ /(4.*xx1*KK*PP/(xx-B)-1.-sqrt(1.+8.*xx1*KK*PP/(xx-B))))
$ /(xx-B)**2.-2.*A*(xx+B)/(xx**2.+2.*B*xx-B**2.)**2.
$ +xx1**2.*KK*PP/(xx-B)**2.*(6.-2.*sqrt(1.+8.*xx1*KK*PP/(xx-B))
$ +8.*(xx1*KK*PP/(xx-B)-1.)/sqrt(1.+8.*xx1*KK*PP/(xx-B)))
$ /(4*xx1*KK*PP/(xx-B)-1.-sqrt(1.+8.*xx1*KK*PP/(xx-B)))
$ **2./(xx-B)
 IF (sym.EQ.1) THEN
 xini=1.0001*B
 ELSE
 xini=0.9
 ENDIF
 es=1.e-4
 maxi=100000000
 err = 100.
 i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
   xxnew = xini - (F(xini)/DER(xini))
   if (xxnew.ne.0.) then
     err = abs((xxnew - xini)/xxnew) * 100.
   endif
   xini = xxnew
   i = i + 1
   go to 10
```

```
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
        write(*,*) 'The root is not reached within the error limit
     $      after prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
        elseif(DER(xini).eq.0.) then
        write(*,*) 'Newton''s method fails....Derivative equal to zero'
      endif
      return
      end
```

B3. Calculations of Excess Molar Enthalpy of Associating Mixtures from Model PPR-3

For Binary Mixtures

```
C     This program allows you to calculate the excess molar enthalpies
C     of associating mixtures using Model PPR-3
C     Component 1 is associating substance
C     Component 2 is non-associating substance
C     test alkanol(1)+hydrocarbon(2) system
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,N)
      DIMENSION x1(70),x2(70),AL(70),BL(70)
      DIMENSION aam(70),bbm(70),deraam(70),derbbm(70)
      DIMENSION vm(70),ZL(70),deltaHM(70)
      DIMENSION HEexp(70),HEcal(70),errHE(70)
      OPEN(11,FILE='input.txt',status='old')
      OPEN(17,file='output.txt',status='old')
      Read(11,*) ww1,ww2,ww3
      READ(11,*) HO,H2
      READ(11,*) a11,a12,a13,b11,b12
      READ(11,*) a21,a22,b21
      READ(11,*) P,tt,N
      READ(11,*) (x1(I),HEexp(I),I=1,N)
      R=0.0831439
      T=tt+273.15
      k12=ww1/1000000.*T**2.+ww2/10000.*T+ww3
      write(17,*)' x1exp    HEexp    HEcal     errHE%'
C     Calculate liquid mole fraction
      Do 2 i=1,N
2     x2(i)=1-x1(i)
      K=exp(HO/T+H2)
      a1=a11+a12*sqrt(T)+a13*T
      b1=(b11+b12*sqrt(T))**2.
C     derivative a and b to T for alkanol
      dera1=a12/2./sqrt(T)+a13
      derb1=(b11+b12*sqrt(T))*b12/sqrt(T)
C     parameters for hydrocarbon
      a2=(a21+a22*sqrt(T))**2.
      b2=b21
C     derivative a and b to T for hydrocarbon
```

```
      dera2=(a21+a22*sqrt(T))*a22/sqrt(T)
C     find root for alkanols
      BL1=b1*P/R/T
      AL1=a1*P/(R*T)**2.0
      CALL NEWRAP1(AL1,BL1,K,P,ZL1)
      v1=ZL1*R*T/P
C     find root for hydrocarbon
      BL2=b2*P/R/T
      AL2=a2*P/(R*T)**2.0
      CALL NEWRAP2(AL2,BL2,ZL2)
      v2=ZL2*R*T/P
C     Calculate HE for two pure components, change HE unit to J/mol
      deltaH1=(P*v1-R*T+(dera1*T-a1)/2./sqrt(2.)/b1
     $       *log((v1+b1+sqrt(2.)*b1)/(v1+b1-sqrt(2.)*b1))
     $     +(2./(1.+sqrt(1.+4.*K*R*T/(v1-b1)))-1.)*R*(HO-T)
     $       +T*derb1/2./K*(1.-sqrt(1.+4.*K*R*T/(v1-b1)))
     $     +a1*T*derb1/b1*(v1/(v1*v1+2.*b1*v1-b1*b1)+1./2./sqrt(2.)/b1
     $       *log((v1+b1-sqrt(2.)*b1)/(v1+b1+sqrt(2.)*b1))))*100.
      deltaH2=(P*v2-R*T+(dera2*T-a2)/2./sqrt(2.)/b2
     $       *log((v2+b2+sqrt(2.)*b2)/(v2+b2-sqrt(2.)*b2)))*100.
      Do 4 i=1,N
C     parameters for mixtures
      aam(i)=x1(i)**2.0*a1+2.0*x1(i)*x2(i)*sqrt(a1*a2)*(1.-k12)
     $         +x2(i)**2.0*a2
      bbm(i)=x1(i)*b1+x2(i)*b2
      BL(i)=bbm(i)*P/R/T
      AL(i)=aam(i)*P/(R*T)**2.0
C     Solve compressibility factor for liquid
      CALL NEWRAPM(AL(i),BL(i),x1(i),x2(i),K,P,ZL(i))
      vm(i)=ZL(i)*R*T/P
C     derivative aal and bbl to T
      deraam(i)=x1(i)**2.*dera1+x1(i)*x2(i)*(1.-k12)
C     *(dera1*a2+dera2*a1)/sqrt(a1*a2)+x2(i)**2.*dera2
      derbbm(i)=x1(i)*derb1
C     Calculate VE and HE for mixture, change HE unit to J/mol
      deltaHM(i)=(P*vm(i)-R*T+(deraam(i)*T-aam(i))/2./sqrt(2.)/bbm(i)
     $       *log((vm(i)+bbm(i)+sqrt(2.)*bbm(i))
     $     /(vm(i)+bbm(i)-sqrt(2.)*bbm(i)))
     $     +(2./(1.+sqrt(1.+4.*K*R*T*x1(i)/(vm(i)-bbm(i))))-1.)*R*x1(i)
     $     *(HO-T)+T*derbbm(i)/2./K*(1.-sqrt(1.+4.*K*R*T*x1(i)
     $     /(vm(i)-bbm(i))))-x2(i)*R*T*T*derbbm(i)/(vm(i)-bbm(i))
     $     +aam(i)*T*derbbm(i)/bbm(i)*(vm(i)/(vm(i)**2.+2.*bbm(i)*vm(i)
     $     -bbm(i)**2.)+1./2./sqrt(2.)/bbm(i)
     $       *log((vm(i)+bbm(i)-sqrt(2.)*bbm(i))
     $     /(vm(i)+bbm(i)+sqrt(2.)*bbm(i)))))*100.
c     Calculate excess properties
      HEcal(i)=deltaHM(i)-x1(i)*deltaH1-x2(i)*deltaH2
      errHE(i)=(HEcal(i)-HEexp(i))/HEexp(i)*100.
C     print the results
      write(17,91)x1(i),HEexp(i),HEcal(i),errHE(i)
4     continue
      DHE=0.0
      AVE=0.0
      RMS=0.0
      Do 8 j=1,N
      AVE=AVE+abs((HEcal(j)-HEexp(j))/HEexp(j))*100.
      DHE=DHE+((HEcal(j)-HEexp(j))/HEexp(j))**2.
```

```
8     RMS=RMS+(HEcal(j)-HEexp(j))**2.
      AVE=AVE/N
      OF=DHE/N
      RMS=sqrt(RMS/N)
      write(17,*)' t/C   P/bar    k12     AvHE%  RMS(J/mol) OF'
      write(17,92) T-273.15,P,k12,AVE,RMS,OF
91    format(1x,f6.4,2x,f7.2,2x,f9.3,2x,f7.3)
92    format(1x,f6.2,1x,f6.4,2x,f6.4,2x,f6.3,2x,f8.4,2x,f6.4)
      END

      SUBROUTINE NEWRAP1(A,B,KK,PP,xx)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      F(xx)=1-2./(1.+sqrt(1.+4.*KK*PP/(xx-B)))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
      DER(xx)=2./(1.+sqrt(1.+(4.*KK*PP/(xx-B))))
     $/(xx-B)**2.0-4.0*KK*PP/(xx-B)**3.0/(1.+sqrt(1.+4.*KK*PP
     $/(xx-B)))**2./sqrt(1.+4.*KK*PP/(xx-B))-2.0*A*(xx+B)
     $      /(xx**2.0+2*B*xx-B**2.0)**2.
      xini=1.001*B
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
       write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
       write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end

      SUBROUTINE NEWRAP2(A,B,xx)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      F(xx)=xx**3.+(B-1.)*xx*xx+(A-3.*B*B-2.*B)*xx+B**3.+B*B-A*B
      DER(xx)=3.*xx*xx+2.*(B-1.)*xx+A-3.*B*B-2.*B
      xini=1.001*B
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
```

```
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20     continue
       if((err.lt.es).and.(DER(xini).ne.0.)) then
       xx=xini
       elseif((err.gt.es).and.(DER(xini).ne.0.)) then
        write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
       elseif(DER(xini).eq.0.) then
        write(*,*) 'Newton''s method fails....Derivative equal to zero.'
       endif
       return
       end

       SUBROUTINE NEWRAPM(A,B,xx1,xx2,KK,PP,xx)
       IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
       F(xx)=1.-(xx2+2.*xx1/(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B))))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
       DER(xx)=(xx2+2.*xx1/(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B))))
     $      /(xx-B)**2.0-4.0*xx1**2.0*KK*PP/(xx-B)**3.0
     $      /(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B)))**2.0
     $      /sqrt(1.+4.*KK*PP*xx1/(xx-B))-2.0*A*(xx+B)
     $      /(xx**2.0+2.*B*xx-B**2.0)**2.
       xini=1.001*B
       es=1.e-8
       maxi=1000
       err = 100.
       i = 1
10     if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20     continue
       if((err.lt.es).and.(DER(xini).ne.0.)) then
       xx=xini
       elseif((err.gt.es).and.(DER(xini).ne.0.)) then
        write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
       elseif(DER(xini).eq.0.) then
        write(*,*) 'Newton''s method fails....Derivative equal to zero.'
```

```
      endif
      return
      end
```

For Ternary Mixtures

```
C     This program allows you to calculate the excess molar enthalpies
C     of associating mixtures using Model PPR-3
C     Component 1 is associating substance
C     Component 2 and 3 are non-associating substances
C     test alkanol(1)+hydrocarbon(2)+hydrocarbon(3) system
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,N)
      DIMENSION x1(70),x2(70),x3(70),AL(70),BL(70)
      DIMENSION aam(70),bbm(70),deraam(70),derbbm(70)
      DIMENSION vm(70),ZL(70),deltaHM(70)
      DIMENSION HEexp(70),HEcal(70),errHE(70)
      OPEN(11,FILE='input.txt',status='old')
      OPEN(17,file='output.txt',status='old')
      Read(11,*) ww1,ww2,ww3
      Read(11,*) ww4,ww5,ww6
      Read(11,*) k23
      READ(11,*) HO,H2
      READ(11,*) a11,a12,a13,b11,b12
      READ(11,*) a21,a22,b21
      READ(11,*) a31,a32,b31
      READ(11,*) P,tt,N
      READ(11,*) ratio
      READ(11,*) (x1(I),HEexp(I),I=1,N)
      R=0.0831439
      T=tt+273.15
      k12=ww1/1000000.*T**2.+ww2/10000.*T+ww3
      k13=ww4/1000000.*T**2.+ww5/10000.*T+ww6
      write(17,*)' x1exp    HEexp    HEcal     errHE%'
      Do 2 i=1,N
      x3(i)=(1-x1(i))/(1.+ratio)
2     x2(i)=1-x1(i)-x3(i)
      K=exp(HO/T+H2)
      a1=a11+a12*sqrt(T)+a13*T
      b1=(b11+b12*sqrt(T))**2.
      dera1=a12/2./sqrt(T)+a13
      derb1=(b11+b12*sqrt(T))*b12/sqrt(T)
      a2=(a21+a22*sqrt(T))**2.
      b2=b21
      dera2=(a21+a22*sqrt(T))*a22/sqrt(T)
      a3=(a31+a32*sqrt(T))**2.
      b3=b31
      dera3=(a31+a32*sqrt(T))*a32/sqrt(T)
      BL1=b1*P/R/T
      AL1=a1*P/(R*T)**2.0
      CALL NEWRAP1(AL1,BL1,K,P,ZL1)
      v1=ZL1*R*T/P
      BL2=b2*P/R/T
      AL2=a2*P/(R*T)**2.0
      CALL NEWRAP2(AL2,BL2,ZL2)
      v2=ZL2*R*T/P
      BL3=b3*P/R/T
      AL3=a3*P/(R*T)**2.0
```

```
      CALL NEWRAP2(AL3,BL3,ZL3)
      v3=ZL3*R*T/P
      deltaH1=(P*v1-R*T+(dera1*T-a1)/2./sqrt(2.)/b1
     $       *log((v1+b1+sqrt(2.)*b1)/(v1+b1-sqrt(2.)*b1))
     $     +(2./(1.+sqrt(1.+4.*K*R*T/(v1-b1)))-1.)*R*(HO-T)
     $       +T*derb1/2./K*(1.-sqrt(1.+4.*K*R*T/(v1-b1)))
     $     +a1*T*derb1/b1*(v1/(v1*v1+2.*b1*v1-b1*b1)+1./2./sqrt(2.)/b1
     $       *log((v1+b1-sqrt(2.)*b1)/(v1+b1+sqrt(2.)*b1))))*100.
      deltaH2=(P*v2-R*T+(dera2*T-a2)/2./sqrt(2.)/b2
     $       *log((v2+b2+sqrt(2.)*b2)/(v2+b2-sqrt(2.)*b2)))*100.
      deltaH3=(P*v3-R*T+(dera3*T-a3)/2./sqrt(2.)/b3
     $       *log((v3+b3+sqrt(2.)*b3)/(v3+b3-sqrt(2.)*b3)))*100.
      Do 4 i=1,N
      aam(i)=x1(i)**2.0*a1+2.0*x1(i)*x2(i)*sqrt(a1*a2)*(1.-k12)
     $         +2.0*x1(i)*x3(i)*sqrt(a1*a3)*(1.-k13)+2.0*x2(i)*x3(i)
     $       *sqrt(a2*a3)*(1.-k23)+x2(i)**2.0*a2+x3(i)**2.0*a3
      bbm(i)=x1(i)*b1+x2(i)*b2+x3(i)*b3
      BL(i)=bbm(i)*P/R/T
      AL(i)=aam(i)*P/(R*T)**2.0
      CALL NEWRAPM(AL(i),BL(i),x1(i),x2(i),x3(i),K,P,ZL(i))
      vm(i)=ZL(i)*R*T/P
      deraam(i)=x1(i)**2.*dera1+x1(i)*x2(i)*(1.-k12)
     $*(dera1*a2+dera2*a1)/sqrt(a1*a2)+x1(i)*x3(i)
     $*(1.-k13)*(dera1*a3+dera3*a1)/sqrt(a1*a3)+x2(i)*x3(i)
     $*(1.-k23)*(dera2*a3+dera3*a2)/sqrt(a2*a3)+x2(i)**2.*dera2
     $+x3(i)**2.*dera3
      derbbm(i)=x1(i)*derb1
      deltaHM(i)=(P*vm(i)-R*T+(deraam(i)*T-aam(i))/2./sqrt(2.)/bbm(i)
     $*log((vm(i)+bbm(i)+sqrt(2.)*bbm(i))/(vm(i)+bbm(i)-
     $sqrt(2.)*bbm(i)))+(2./(1.+sqrt(1.+4.*K*R*T*x1(i)/(vm(i)-
     $bbm(i))))-1.)*R*x1(i)*(HO-T)+T*derbbm(i)/2./K*(1.-
     $sqrt(1.+4.*K*R*T*x1(i)/(vm(i)-bbm(i))))-(x2(i)+x3(i))
     $*R*T*T*derbbm(i)/(vm(i)-bbm(i))+aam(i)*T*derbbm(i)/bbm(i)*(vm(i)
     $/(vm(i)**2.+2.*bbm(i)*vm(i)-bbm(i)**2.)+1./2./sqrt(2.)/bbm(i)
     $*log((vm(i)+bbm(i)-sqrt(2.)*bbm(i))
     $/(vm(i)+bbm(i)+sqrt(2.)*bbm(i))))*100.
      HEcal(i)=deltaHM(i)-x1(i)*deltaH1-x2(i)*deltaH2-x3(i)*deltaH3
      errHE(i)=(HEcal(i)-HEexp(i))/HEexp(i)*100.
      write(17,91)x1(i),HEexp(i),HEcal(i),errHE(i)
4     continue
      DHE=0.0
      AVE=0.0
      RMS=0.0
      Do 8 j=1,N
      AVE=AVE+abs((HEcal(j)-HEexp(j))/HEexp(j))*100.
      DHE=DHE+((HEcal(j)-HEexp(j))/HEexp(j))**2.
8     RMS=RMS+(HEcal(j)-HEexp(j))**2.
      AVE=AVE/N
      OF=DHE/N
      RMS=sqrt(RMS/N)
      write(17,*)' t/C    P/bar     k12      AvHE%   RMS(J/mol) OF'
      write(17,92) T-273.15,P,k12,AVE,RMS,OF
91    format(1x,f6.4,2x,f7.2,2x,f9.3,2x,f7.3)
92    format(1x,f6.2,1x,f6.4,2x,f6.4,2x,f6.3,2x,f8.4,2x,f6.4)
      END

      SUBROUTINE NEWRAP1(A,B,KK,PP,xx)
```

```
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      F(xx)=1-2./(1.+sqrt(1.+4.*KK*PP/(xx-B)))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
      DER(xx)=2./(1.+sqrt(1.+(4.*KK*PP/(xx-B))))
     $      /(xx-B)**2.0-4.0*KK*PP/(xx-B)**3.0
     $      /(1.+sqrt(1.+4.*KK*PP/(xx-B)))**2.0
     $      /sqrt(1.+4.*KK*PP/(xx-B))-2.0*A*(xx+B)
     $      /(xx**2.0+2*B*xx-B**2.0)**2.
      xini=1.001*B
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
       write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
       write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end

      SUBROUTINE NEWRAP2(A,B,xx)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      F(xx)=xx**3.+(B-1.)*xx*xx+(A-3.*B*B-2.*B)*xx+B**3.+B*B-A*B
      DER(xx)=3.*xx*xx+2.*(B-1.)*xx+A-3.*B*B-2.*B
      xini=1.001*B
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
```

```
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
       write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
       write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end

      SUBROUTINE NEWRAPM(A,B,xx1,xx2,xx3,KK,PP,xx)
      IMPLICIT REAL*8(A-H,K,O-Z),INTEGER (I,J,L,m,N)
      F(xx)=1.-(xx2+xx3+2.*xx1/(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B))))
     $      /(xx-B)+A/(xx**2.0+2.0*B*xx-B**2.0)
      DER(xx)=(xx2+xx3+2.*xx1/(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B))))
     $      /(xx-B)**2.0-4.0*xx1**2.0*KK*PP/(xx-B)**3.0
     $      /(1.+sqrt(1.+4.*KK*PP*xx1/(xx-B)))**2.0
     $      /sqrt(1.+4.*KK*PP*xx1/(xx-B))-2.0*A*(xx+B)
     $      /(xx**2.0+2.*B*xx-B**2.0)**2.
      xini=1.001*B
      es=1.e-8
      maxi=1000
      err = 100.
      i = 1
10    if((i.eq.maxi).or.(err.lt.es).or.(DER(xini).eq.0.)) go to 20
        xxnew = xini - (F(xini)/DER(xini))
        if (xxnew.ne.0.) then
          err = abs((xxnew - xini)/xxnew) * 100.
        endif
        xini = xxnew
        i = i + 1
        go to 10
20    continue
      if((err.lt.es).and.(DER(xini).ne.0.)) then
      xx=xini
      elseif((err.gt.es).and.(DER(xini).ne.0.)) then
       write(*,*) 'The root is not reached within the error limit after
     $      prescribed number of iteration.'
        write(*,*)
        write(*,*) 'The approximate root =',xini
        write(*,*)
        write(*,*) 'The percentage relative error =',err
      elseif(DER(xini).eq.0.) then
       write(*,*) 'Newton''s method fails....Derivative equal to zero.'
      endif
      return
      end
```

APPENDIX C
FIGURES OF CALCULATED EXCESS PROPERTY RESULTS OF SELECTED SYSTEMS

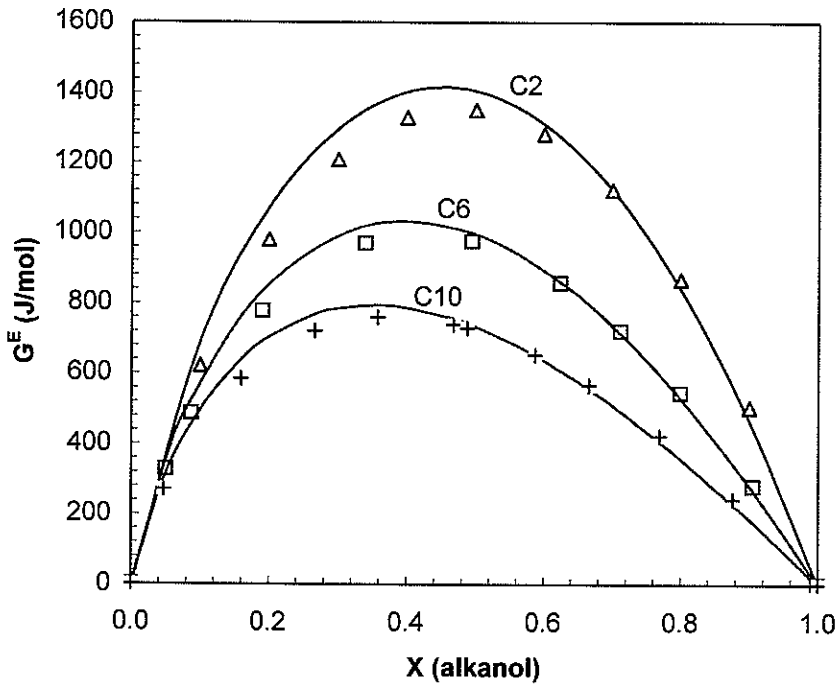

Figure C1: G^E of Alkanol+*n*-Hexane System at 298.15K. Symbols: Experimental Data of Alkanol+*n*-Hexane. Δ: Ethanol(C2)+*n*-Hexane (Smith and Robinson, 1970); □: Hexanol(C6)+*n*-Hexane (Kimura and Benson, 1981); +: Decanol(C10)+*n*-Hexane (Wieczorek, 1979); —: Calculated Values by ERAS Model.

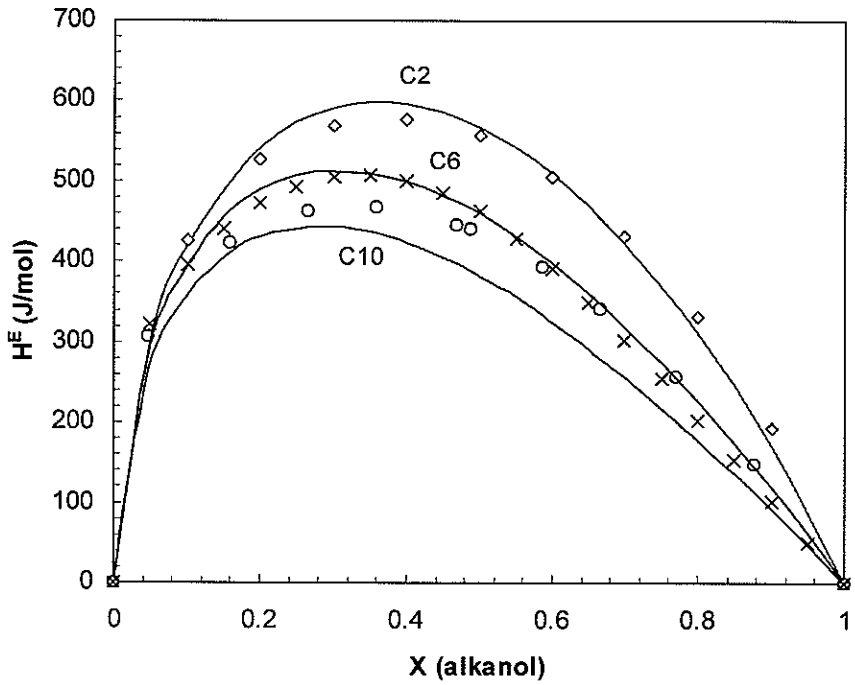

Figure C2a: H^E of Alkanol+*n*-Hexane System at 298.15K. Symbols: Experimental Data of Alkanol+*n*-Hexane. ◊: Ethanol(C2)+*n*-Hexane (Smith and Robinson, 1970); ×: Hexanol(C6)+*n*-Hexane (Wieczorek and Stecki, 1978a); o: Decanol(C10)+*n*-Hexane (Wieczorek, 1979); —: Calculated Values by ERAS Model.

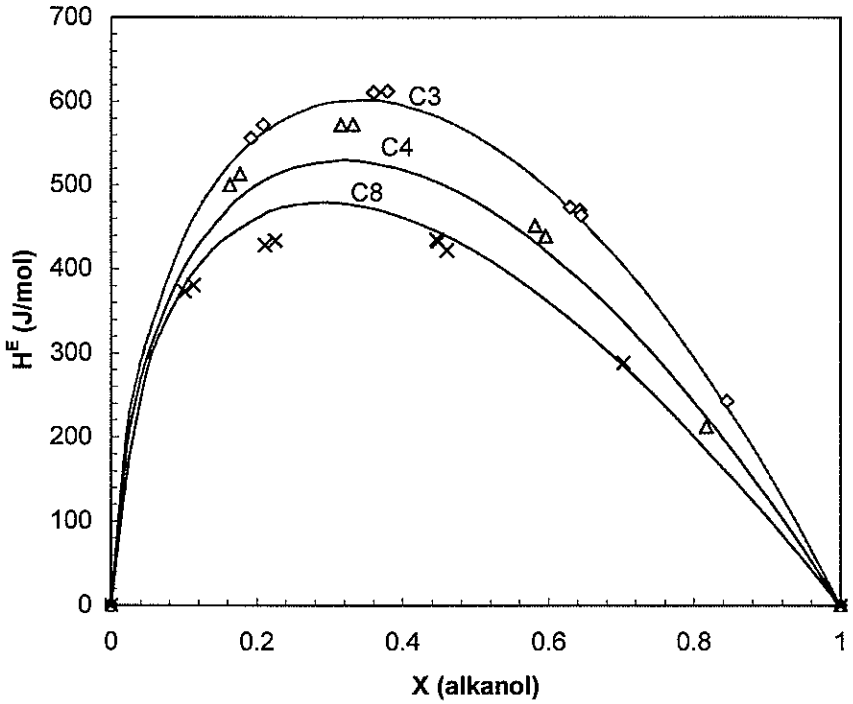

Figure C2b: H^E of Alkanol+*n*-Hexane System at 298.15K. Symbols: Experimental Data (Brown et al., 1964) of Alkanol+*n*-Hexane. ◊: 1-Propanol(C3)+*n*-Hexane; Δ: 1-Butanol(C4)+*n*-Hexane; ×: Octanol(C8)+*n*-Hexane; —: Calculated Values by ERAS Model.

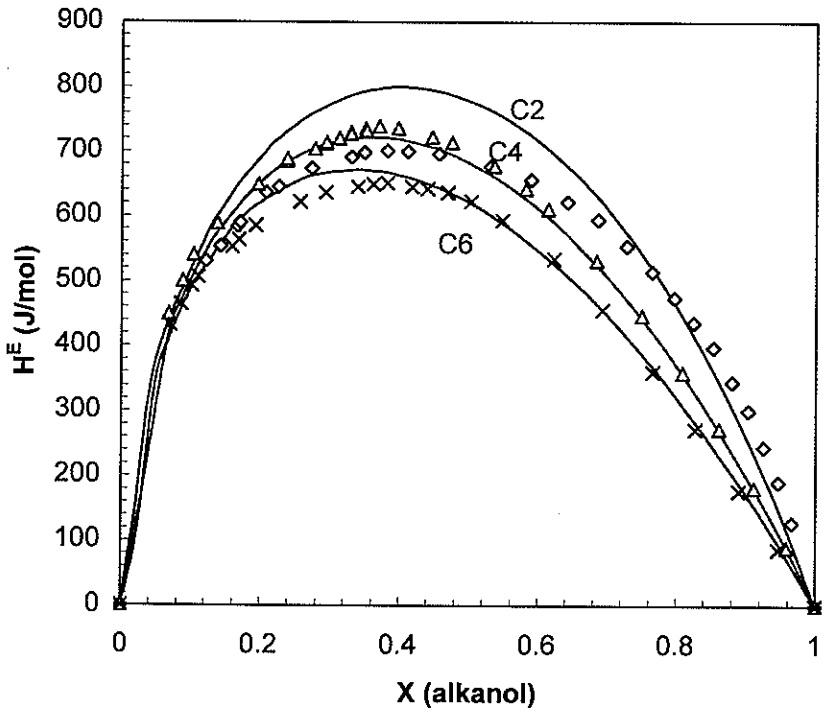

Figure C3a: H^E of Alkanol+*n*-Nonane System at 298.15K. Symbols: Experimental Data (Christensen et al., 1979a) of Alkanol+*n*-Nonane. ◊: Ethanol(C2)+*n*-Nonane; Δ: 1-Butanol(C4)+*n*-Nonane; ×: Hexanol(C6)+*n*-Nonane; —: Calculated Values by ERAS model.

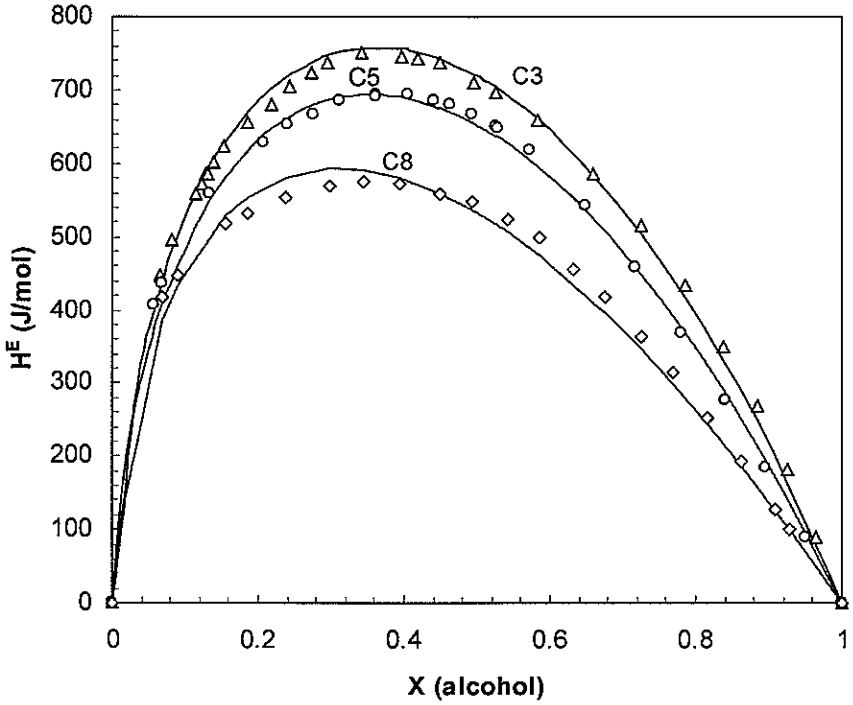

Figure C3b: H^E of Alkanol+*n*-Nonane System at 298.15K. Symbols: Experimental Data (Christensen et al., 1979a) of Alkanol+*n*-Nonane. Δ: 1-Propanol(C3)+*n*-Nonane; o: Pentanol(C5)+*n*-Nonane; ◊: Octanol(C8)+*n*-Nonane; —: Calculated Values by ERAS Model.

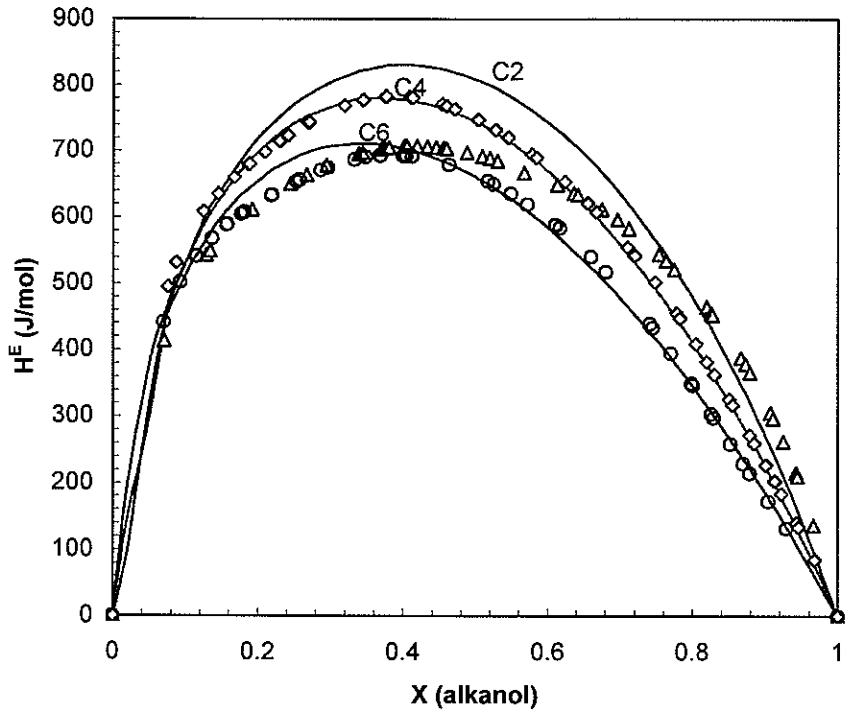

Figure C4a: H^E of Alkanol+*n*-Decane System at 298.15K. Symbols: Experimental Data (Christensen et al., 1979b) of Alkanol+*n*-Decane. Δ: Ethanol(C2)+*n*-Decane; ◊: 1-Butanol(C4)+*n*-Decane; o: Hexanol(C6)+*n*-Decane; —: Calculated Values by ERAS Model.

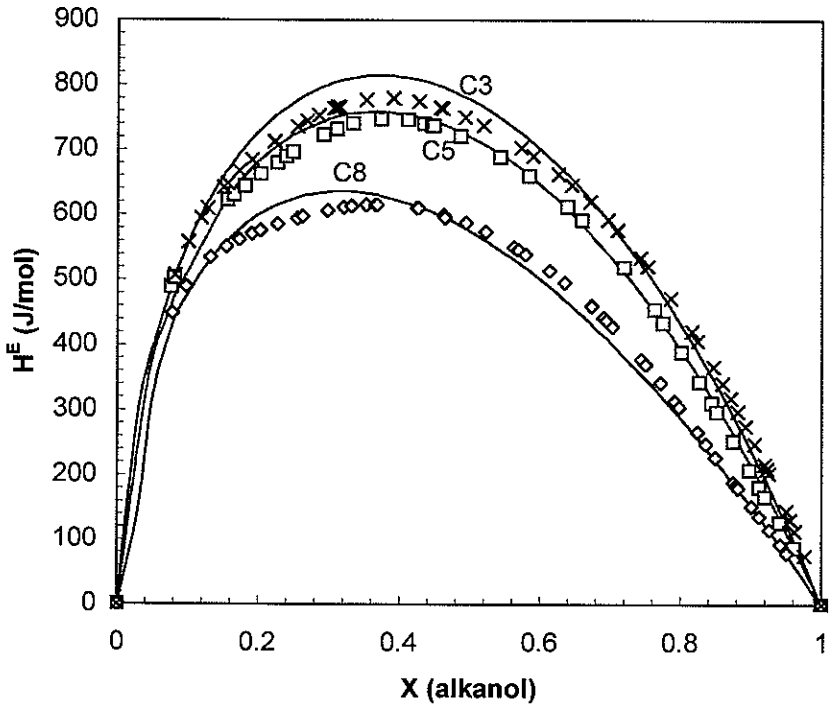

Figure C4b: H^E of Alkanol+*n*-Decane System at 298.15K. Symbols: Experimental Data (Christensen et al., 1979b) of Alkanol+*n*-Decane. ×: 1-Propanol(C3)+*n*-Decane; □: Pentanol(C5)+*n*-Decane; ◊: Octanol(C8)+*n*-Decane; —: Calculated Values by ERAS Model.

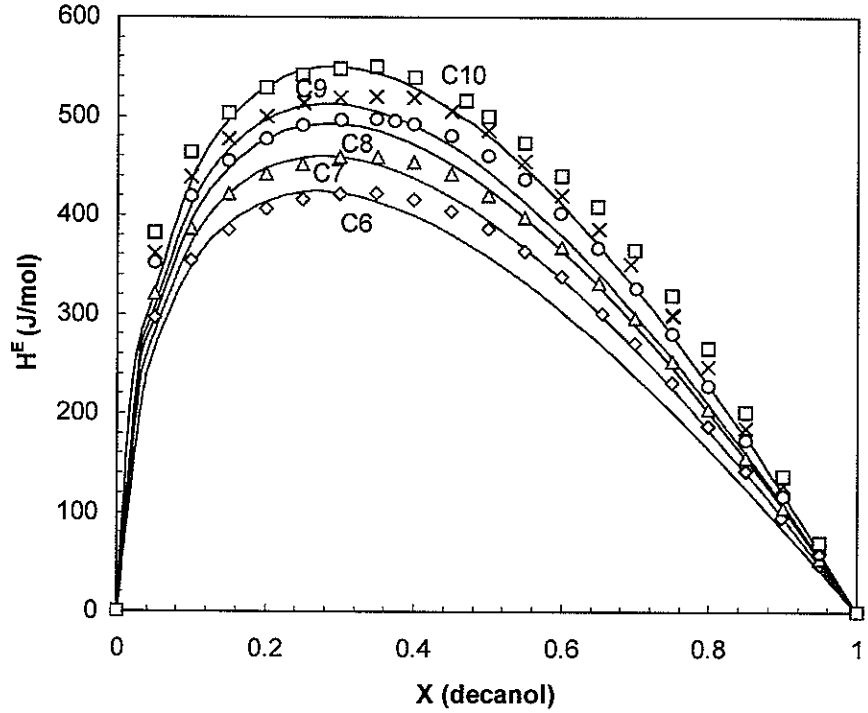

Figure C5: H^E of Decanol+*n*-Alkane System at 298.15K. Symbols: Experimental Data (Kumaran and Benson, 1984) of Decanol+*n*-Alkane. ◊: Decanol+*n*-Hexane(C6); Δ: Decanol+*n*-Heptane(C7); o: Decanol+*n*-Octane(C8); ×: Decanol+*n*-Nonane(C9); □: Decanol+*n*-Decane(C10); —: Calculated Values by ERAS Model.

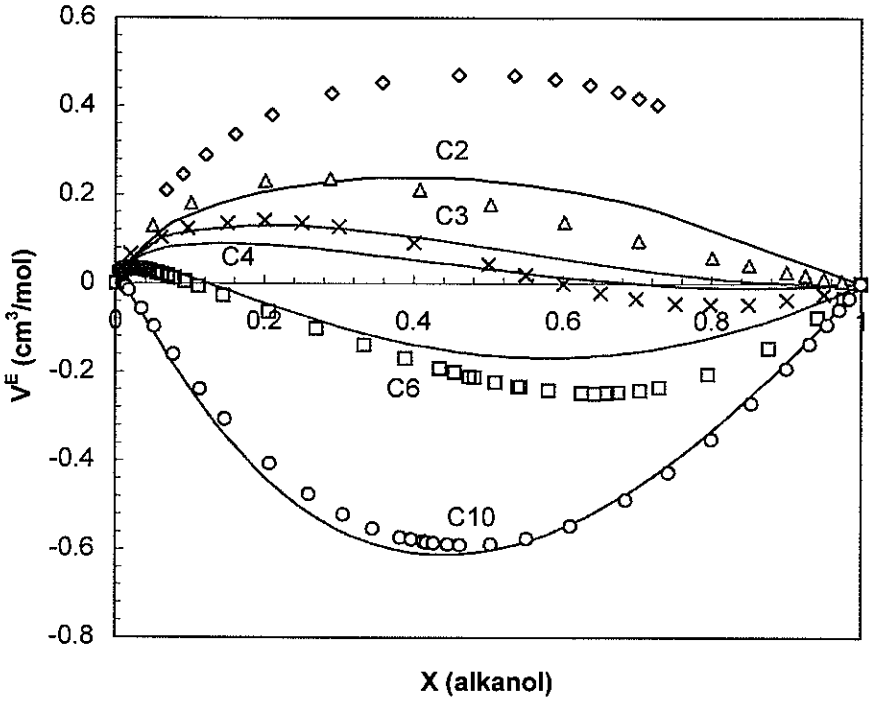

Figure C6: V^E of Alkanol+*n*-Hexane System at 298.15K. Symbols: Experimental Data of Alkanol+*n*-Hexane. ◊: Ethanol(C2)+*n*-Hexane (Treszczanowicz and Benson, 1977); Δ: 1-Propanol(C3)+*n*-Hexane (Heintz et al., 1986b); ×: 1-Butanol(C4)+*n*-Hexane (Heintz et al., 1986b); □: Hexanol(C6)+*n*-Hexane (Heintz et al., 1986b; Treszczanowicz and Benson, 1980); o: Decanol(C10)+*n*-Hexane (Treszczanowicz et al., 1981); —: Calculated Values by ERAS Model.

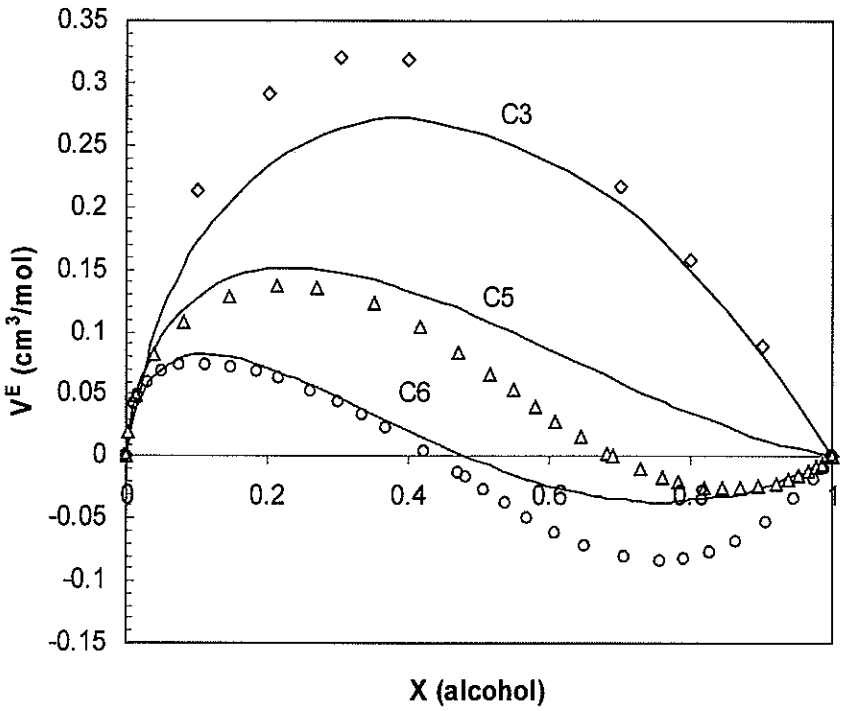

Figure C7: V^E of Alkanol+*n*-Heptane System at 298.15K. Symbols: Experimental Data of Alkanol+*n*-Heptane. ◊: 1-Propanol(C3)+*n*-Heptane (Bender et al., 1991); Δ: Pentanol(C5)+*n*-Heptane (Kaur et al., 1991; Treszczanowicz and Benson, 1978); o: Hexanol(C6)+*n*-Heptane (Treszczanowicz and Benson, 1978); —: Calculated Values by ERAS Model.

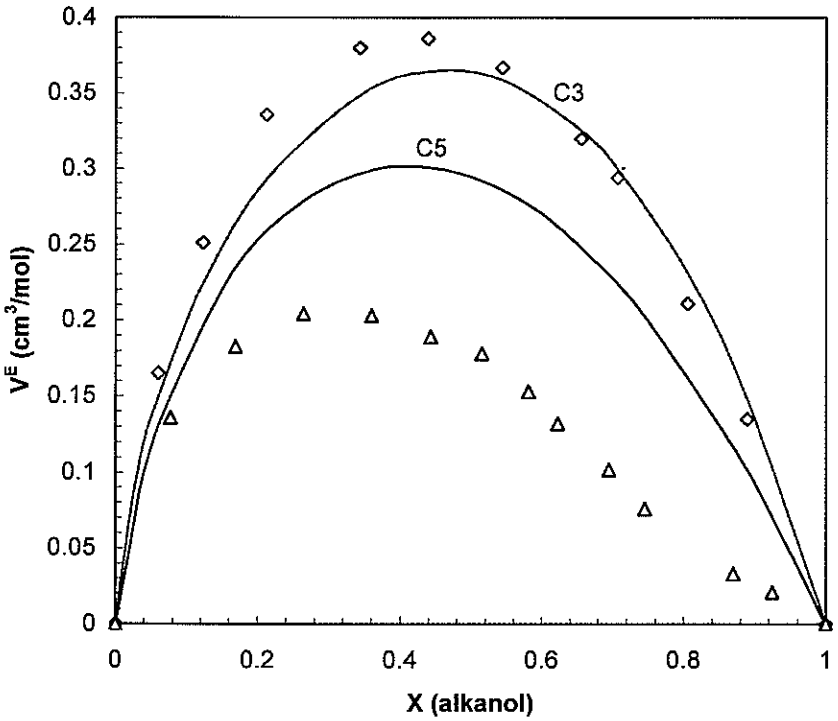

Figure C8: V^E of Alkanol+*n*-Octane System at 298.15K. Symbols: Experimental Data (Kaur et al., 1991) of Alkanol+*n*-Octane. ◊: 1-Propanol(C3)+*n*-Octane; Δ: Pentanol(C5)+*n*-Octane; —: Calculated Values by ERAS Model.

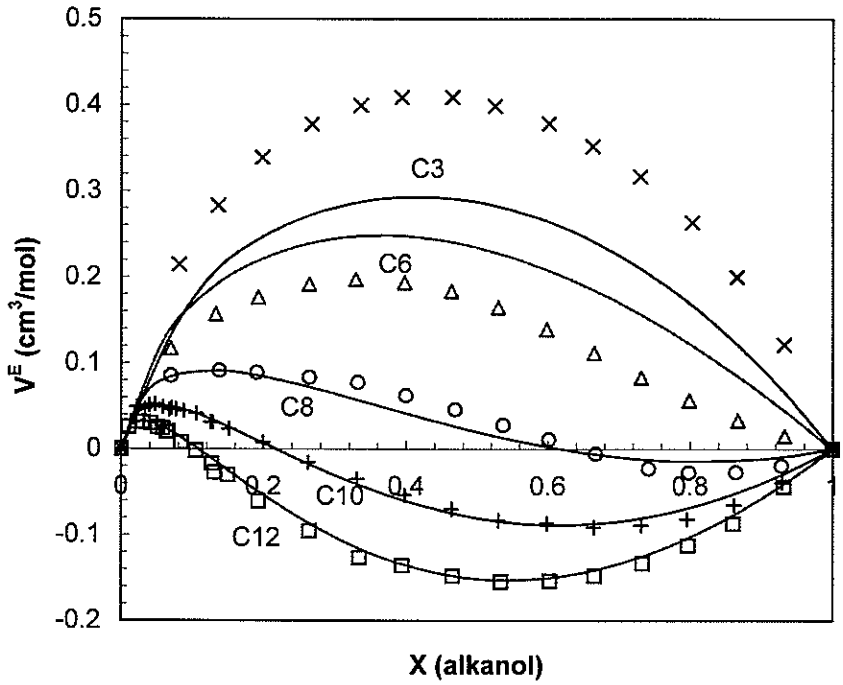

Figure C9: V^E of Alkanol+*n*-Nonane System at 298.15K. Symbols: Experimental Data (Wagner and Heintz, 1986) of Alkanol+*n*-Nonane. ×: 1-Propanol(C3)+*n*-Nonane; Δ: Hexanol(C6)+*n*-Nonane; o: Octanol(C8)+*n*-Nonane; +: Decanol(C10)+*n*-Nonane; □: Dodecanol(C12)+*n*-Nonane; —: Calculated Values by ERAS Model.

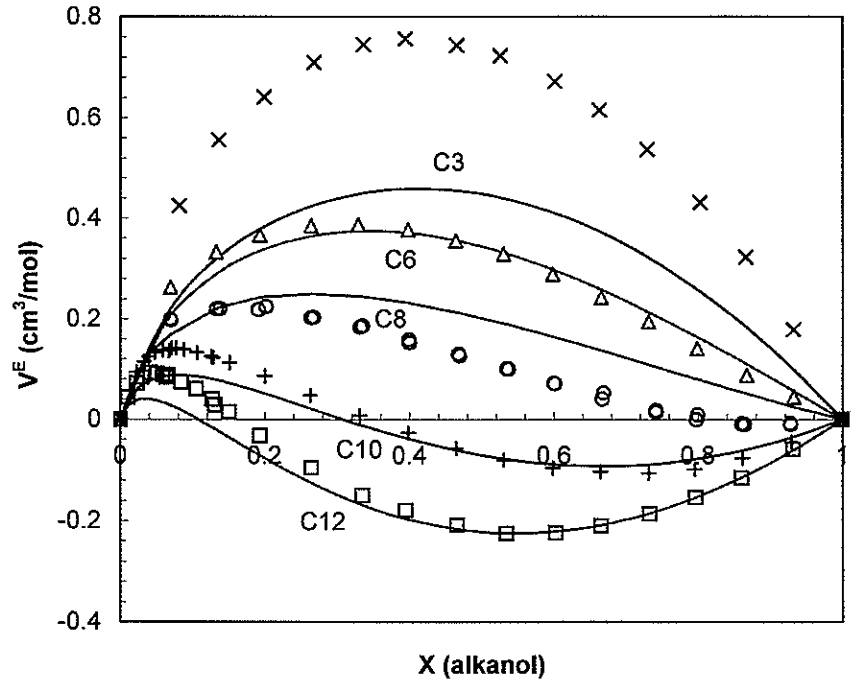

Figure C10: V^E of Alkanol+*n*-Nonane System at 333.15K. Symbols: Experimental Data (Wagner and Heintz, 1986) of Alkanol+*n*-Nonane. ×: 1-Propanol(C3)+*n*-Nonane; Δ: Hexanol(C6)+*n*-Nonane; o: Octanol(C8)+*n*-Nonane; +: Decanol(C10)+*n*-Nonane; □: Dodecanol(C12)+*n*-Nonane; —: Calculated Values by ERAS Model.

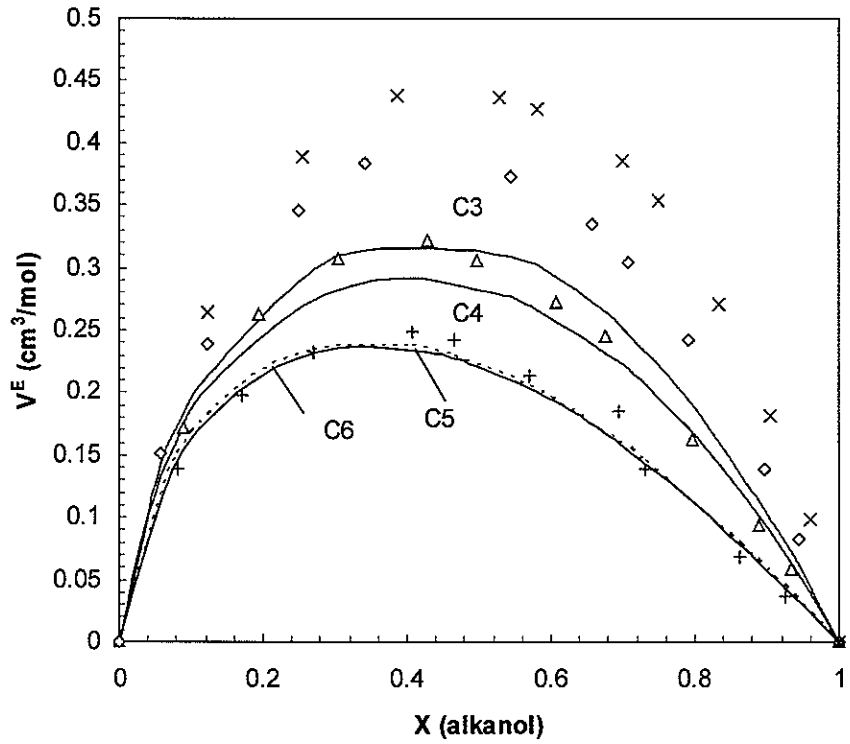

Figure C11: V^E of Alkanol+*n*-Decane System at 298.15K. Symbols: Experimental Data (Kaur et al., 1991) of Alkanol+*n*-Decane; ×: 1-Propanol(C3)+*n*-Decane; ◊: 1-Butanol(C4)+*n*-Decane; Δ: Pentanol(C5)+*n*-Decane; +: Hexanol(C6)+*n*-Decane; —: Calculated Values by ERAS Model; ----: Calculated Values of Hexanol(C6)+*n*-Decane by ERAS Model.

APPENDIX D
FIGURES OF SELECTED CALCULATED VLE RESULTS

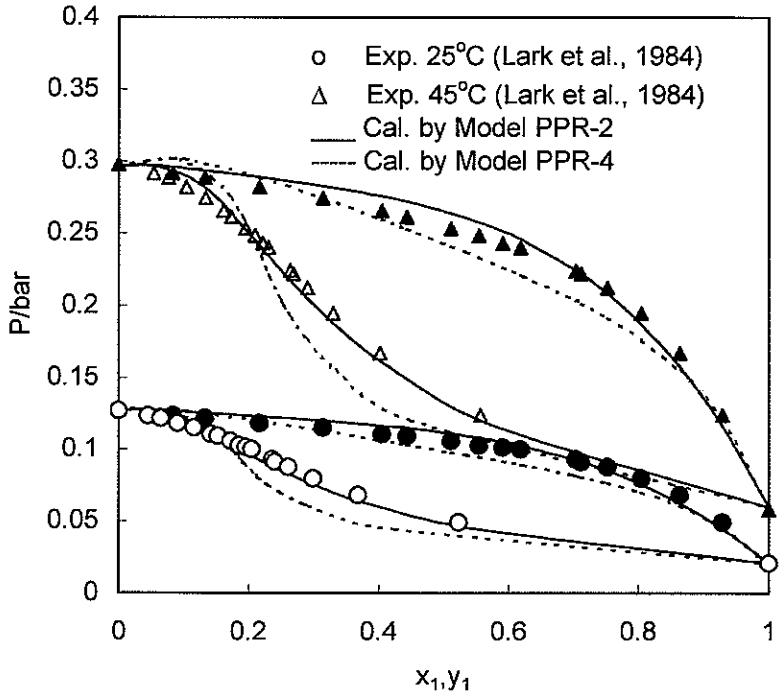

Figure D1: VLE for Acetic acid(1)+Benzene(2) System

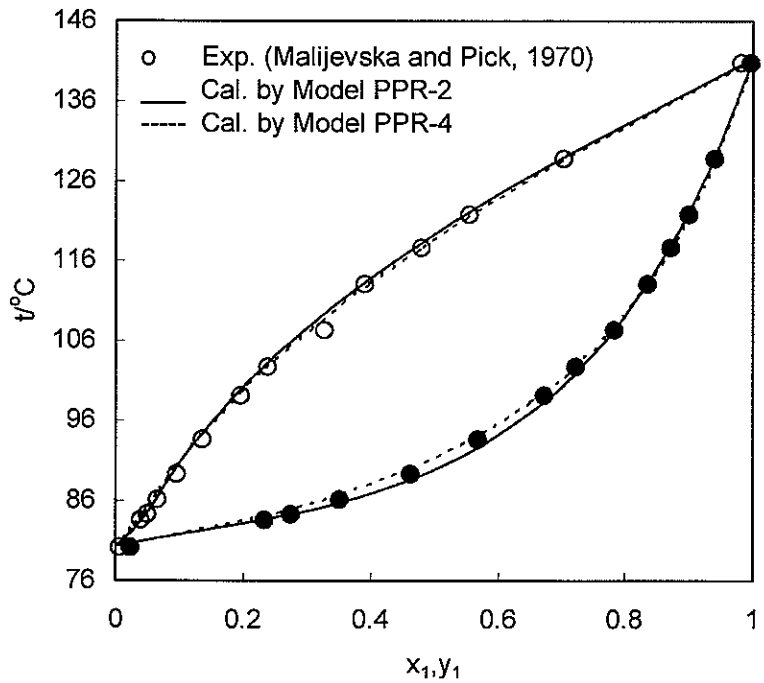

Figure D2: VLE for Propionic acid(1)+Benzene(2) System at 1atm

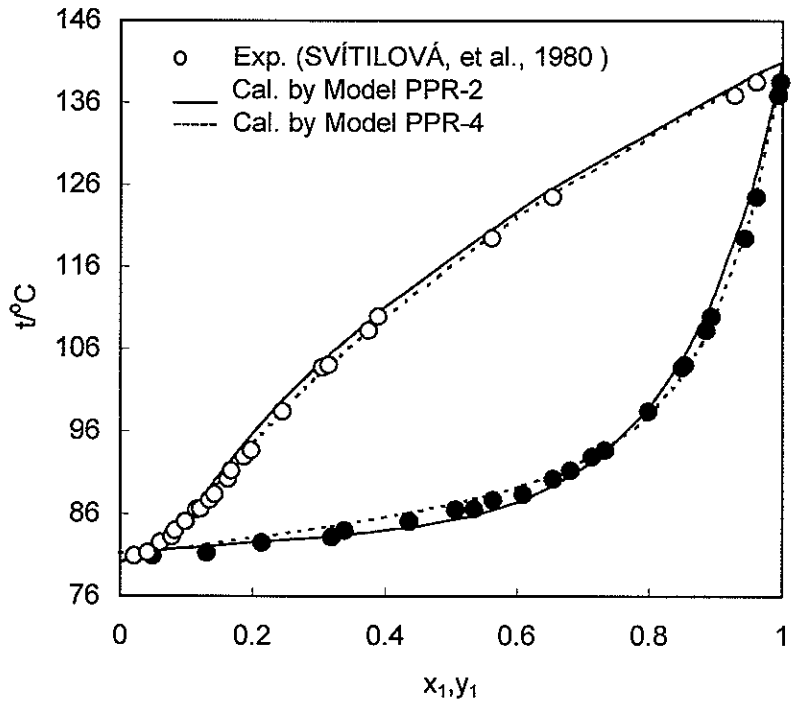

Figure D3: VLE for Propionic acid(1)+Cyclohexane(2) System at 1atm

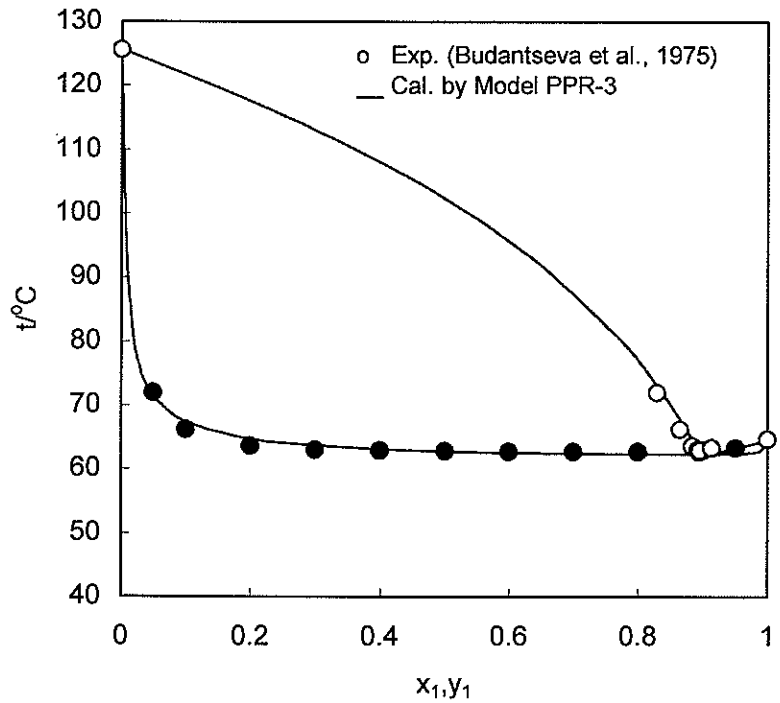

Figure D4: VLE for Methanol(1)+*n*-Octane(2) System at 1 atm

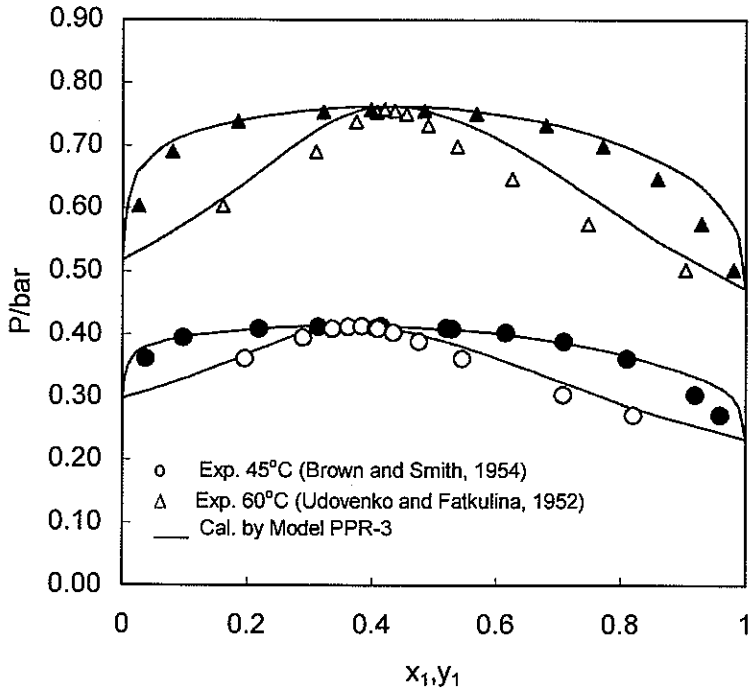

Figure D5: VLE for Ethanol(1)+Benzene(2) System

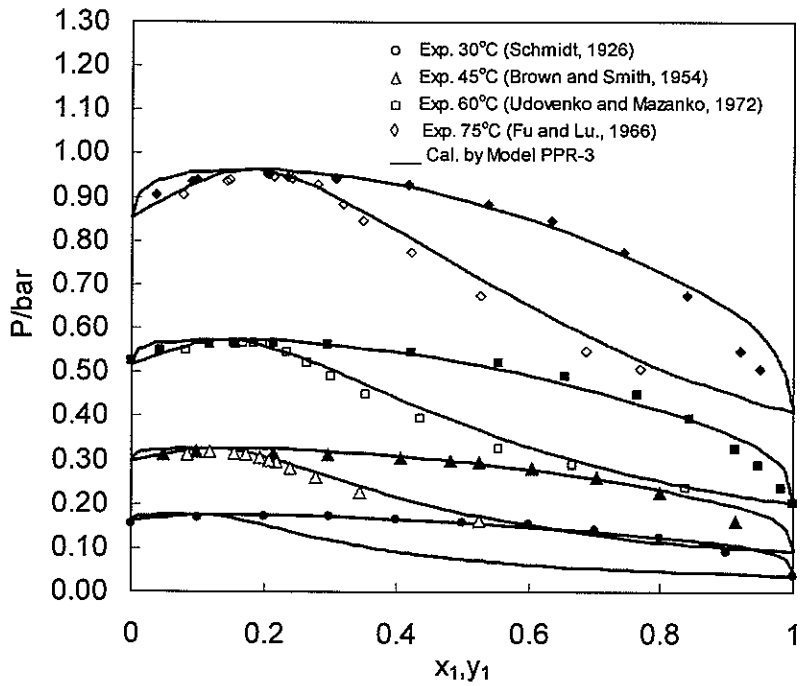

Figure D6: VLE for 1-Propanol(1)+Benzene(2) System

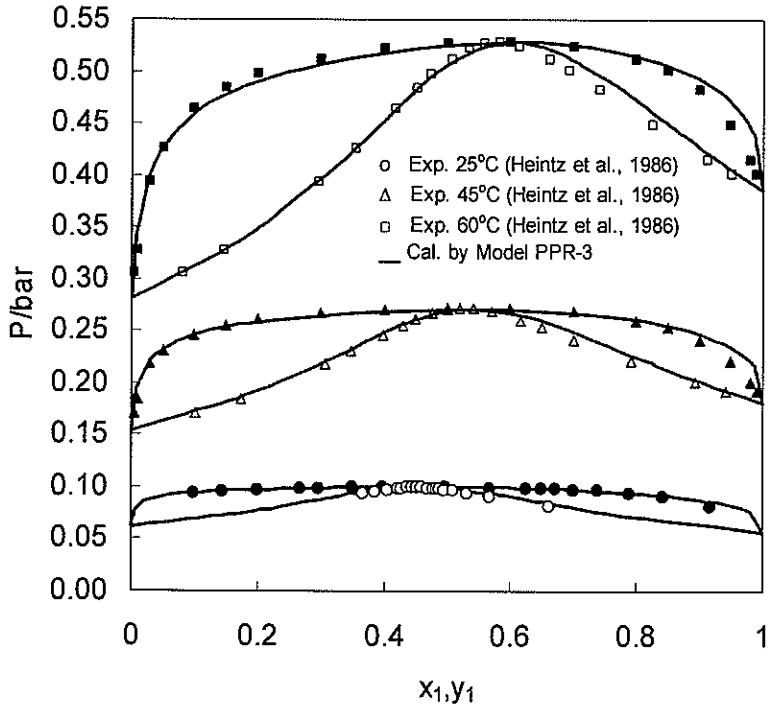

Figure D7: VLE for 2-Propanol(1)+*n*-Heptane(2) System

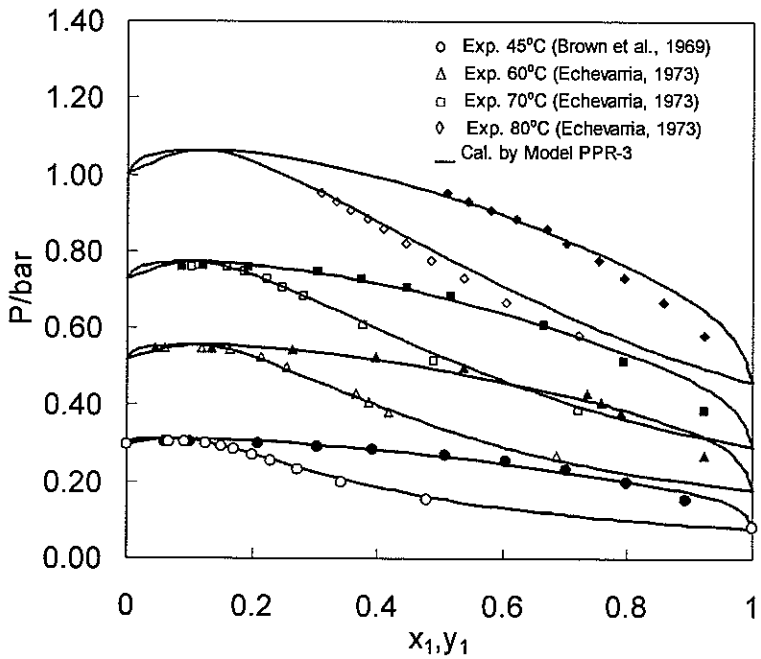

Figure D8: VLE for 2-Butanol(1)+Benzene(2) System

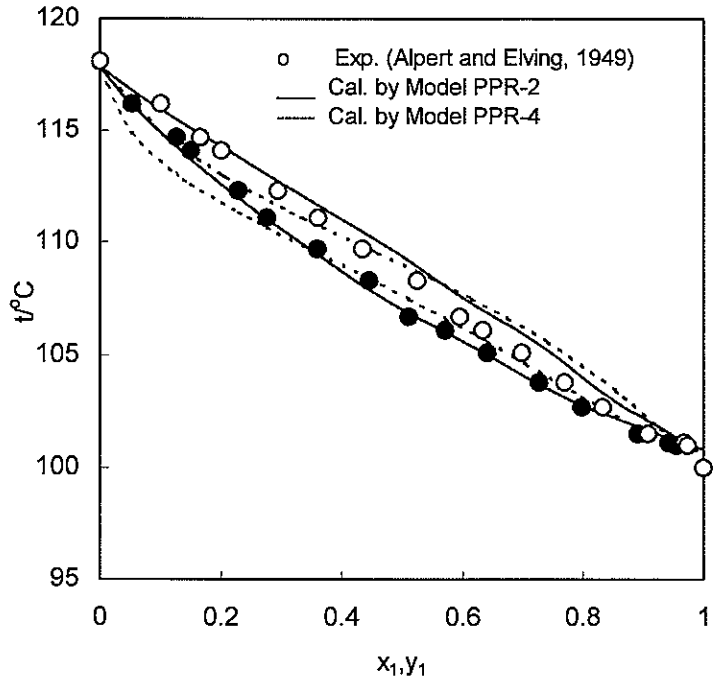

Figure D9: VLE for Formic acid(1)+Acetic acid(2) System at 1atm

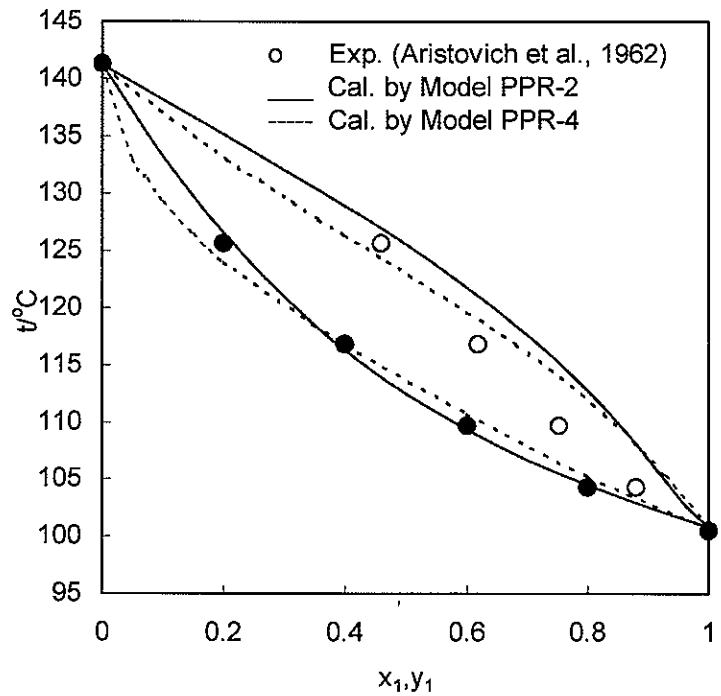

Figure D10: VLE for Formic acid(1)+Propionic acid(2) System at 1atm

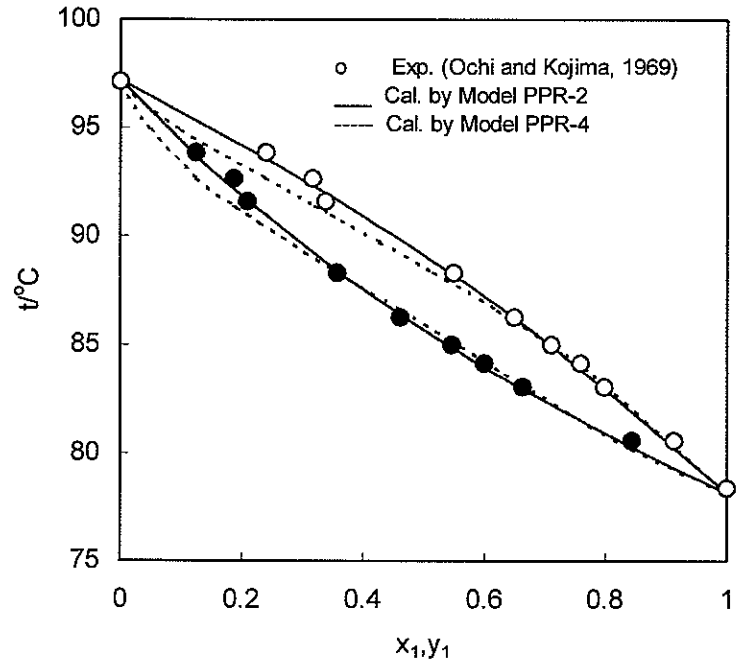

Figure D11: VLE for Ethanol(1)+1-Propanol(2) System at 1atm

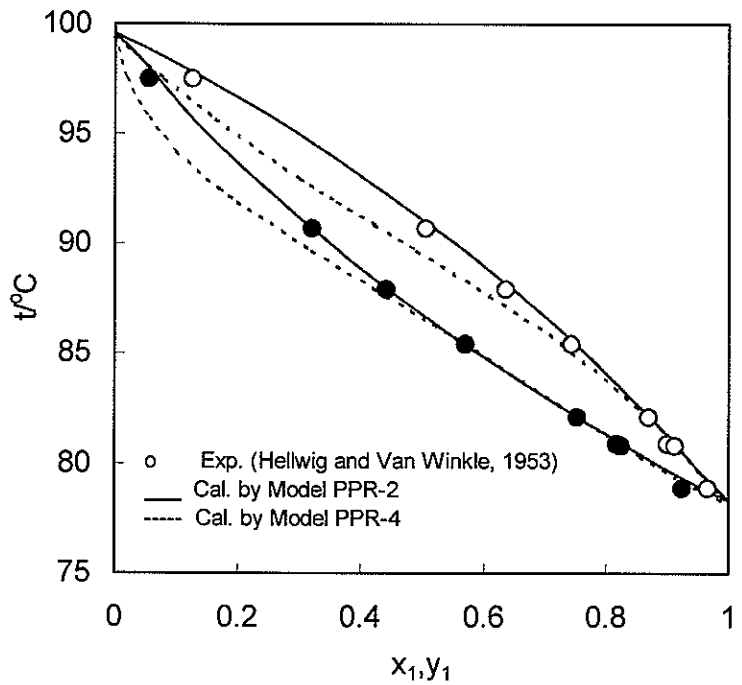

Figure D12: VLE for Ethanol(1)+2-Butanol(2) System at 1atm

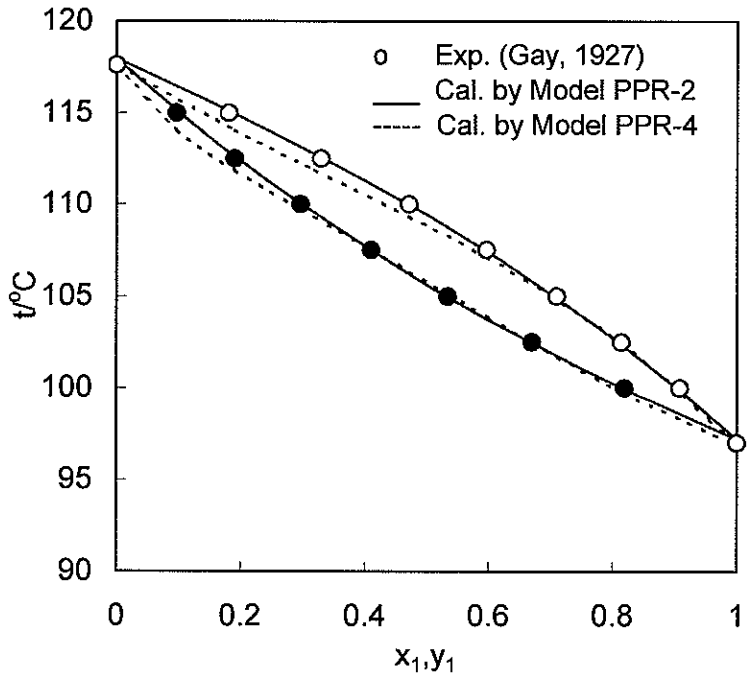

Figure D13: VLE for 1-Propanol(1)+1-Butanol(2) System at 1atm

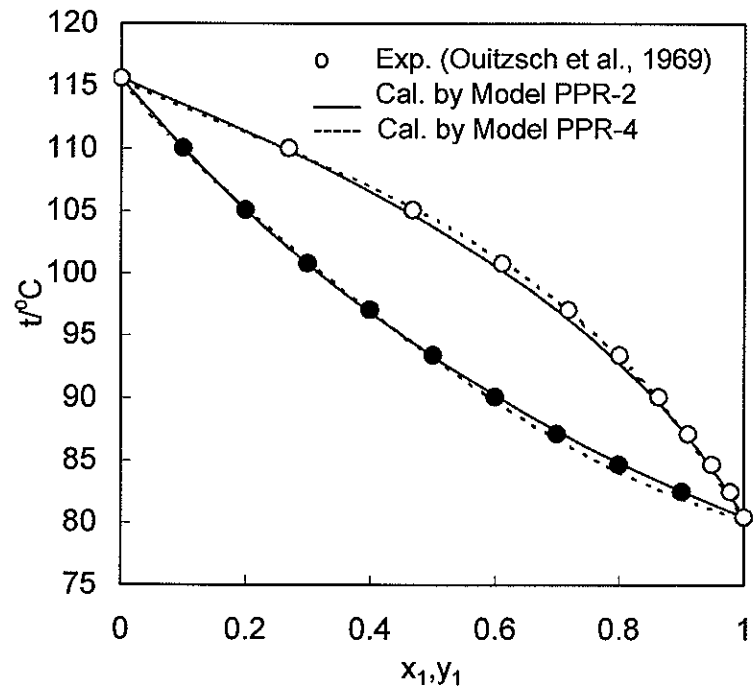

Figure D14: VLE for Tert-butanol(1)+1-Butanol(2) System at 700mmHg

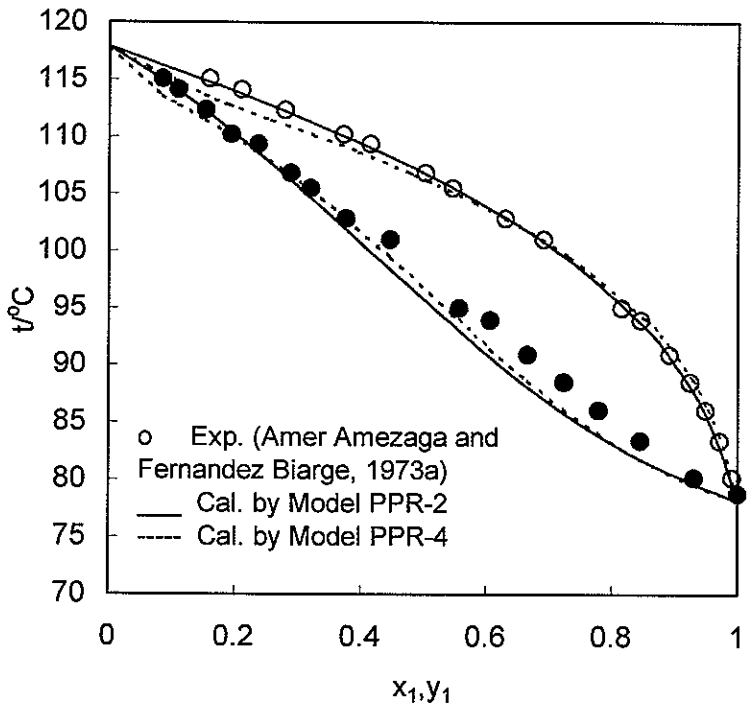

Figure D15: VLE for Ethanol(1)+Acetic acid(2) System at 1 atm

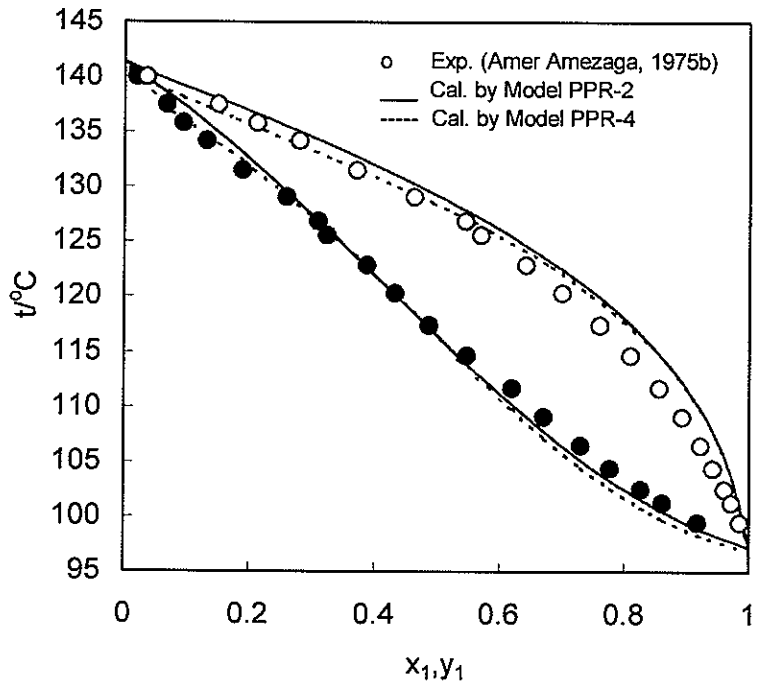

Figure D16: VLE for 1-Propanol(1)+Propionic acid(2) System at 1atm

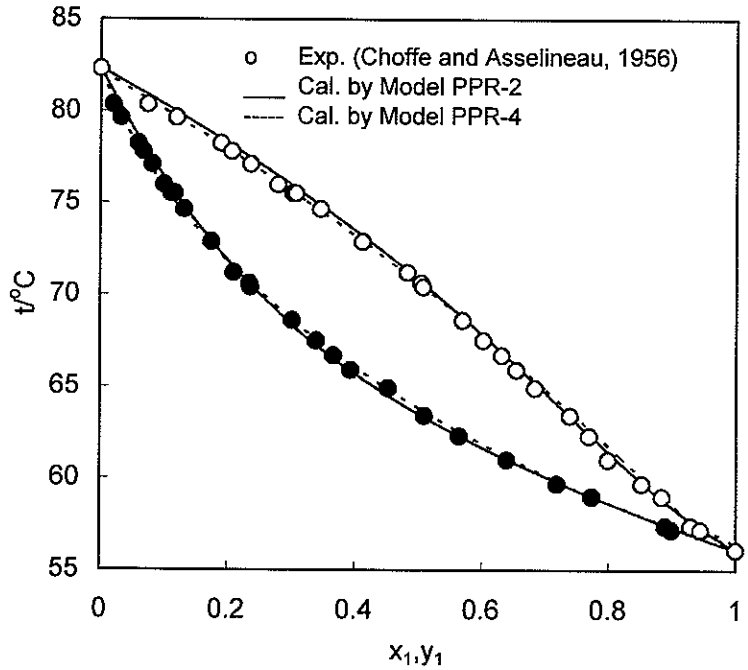

Figure D17: VLE for Acetone(1)+2-Propanol(2) System at 1atm

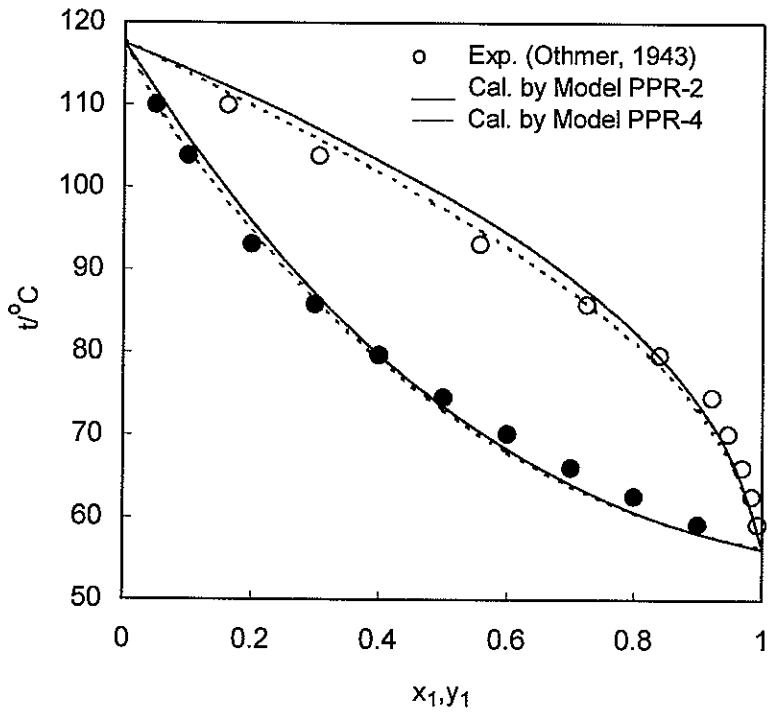

Figure D18: VLE for Acetone(1)+Acetic acid(2) System at 1atm

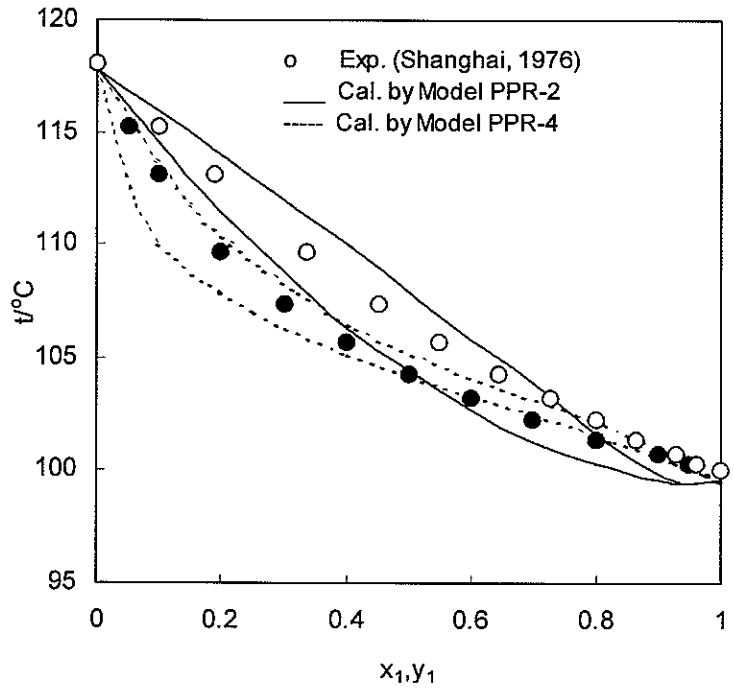

Figure D19: VLE for Water(1)+Acetic acid(2) System at 1atm

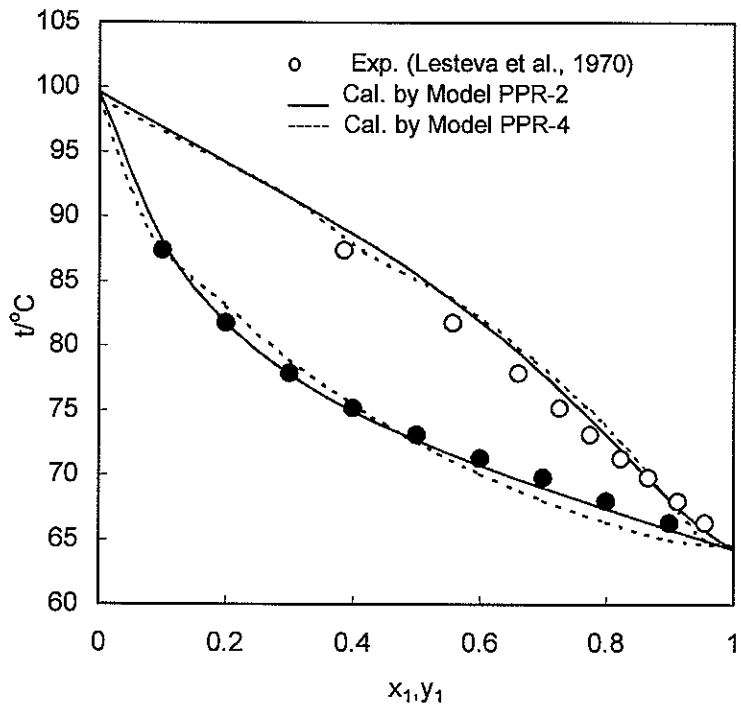

Figure D20: VLE for Methanol(1)+Water(2) System at 1atm

APPENDIX E
CALIBRATION OF SYRINGE PUMP AND DETERMINATION OF CALIBRATION CONSTANT

E1. Calibration of Syringe Pump

A syringe pump (Harvard Apparatus Model 33) is used to deliver the working liquids into the mixing cell of the microcalorimeter. Two stainless steel syringes, each having a capacity of about 46 cm^3, are equipped with water jackets to maintain the fluids inside the syringes at the desired temperatures. The reverse osmosis (RO) water at 25°C is chosen as the calibration fluid with flow rates ranging from 0.3 $ml \cdot h^{-1}$ to 18 $ml \cdot h^{-1}$. Three runs are conducted for each flow rate. For each run, the flow rate of pumping liquids is set and the inside diameter of the syringe and the precise elapsed flow time are recorded. The RO water is collected and weighted after each run, about 30 minutes in duration, and the calibrated flow rate, $f_{calibrated}$, is obtained by dividing the ratio of water mass to water density ρ_{H2O}, which is a function of temperature, by the flow time. The calibration is carried out for two different sizes of syringes (15.63mm OD and 15.635mm OD) and for different flow rates. The results are given in Tables E1 and E2, respectively. On the basis of the calibration measurements made by using RO water as the calibration fluid, the gravimetrically measured flow rates are agreed with the flow rate readings within 0.24% and 0.27%, respectively, for the two syringe pumps.

E2. Calibration Constant for Steady State Heat Generation

Before measuring the heat of mixing or excess molar enthalpy, one must establish the relationship between the heat effect and the amplified thermoelectric output when there is no mixing of fluids. This is determined for each pure liquid at constant temperature, for all the different flow rates of each syringe. A series of output voltage readings E^0 are taken from a digital voltmeter (Hewlett-Packard Model 3457A Multimeter) without applying an electric current input and another series of readings E are taken with applying an electric current input on the order of 10mA to the microcalorimeter cell. The electrical current readings are recorded at the beginning and the end of experiment. An average value of the electrical current readings is taken to

calculate the heat effect W. The calibration constant, ε, can be obtained via the following basic equation for a steady state heat generation:

$$W = \varepsilon(E - E^0) \qquad \text{(E2.1)}$$

The calibration constant, ε, varies with the flow rate and temperature of the liquid. The experimental results of the calibration constants determined at several flow rates for three pure liquids at different temperatures are given in Figures E1 - E3, respectively. It can be seen from Figure E1 that the calibration constant, ε, for ethanol varies linearly with the flow rates f at each temperature. At a fixed flow rate, the higher the temperature, the smaller is the value of the calibration constant. The same trend occurs for *n*-hexane at 25°C and 30°C in Figure E2. However, the curve that is used to describe the variation of calibration constant, ε, for *n*-hexane with volume flow rate f at 40°C intersects the curves at 25°C and 30°C. The reliability of the calibration results at 40°C is probably not as good as that at 25°C and 30°C because of the possible occurrence of very tiny gas bubbles which were not visible to the naked eye.

Table E1: Calibration of the Syringe Pump Using Syringe #615 (15.63 mmOD)

No of Run	f $ml \cdot h^{-1}$	10^3f $cm^3 \cdot s^{-1}$	t °C	ρ_{H2O} $kg \cdot m^{-3}$	Time sec	m_{H2O} g	V_{actual} ml	$f_{calibrated}$ $ml \cdot h^{-1}$	Error %
1	18	5	24.988	997.12	1805.90	9.010	9.0361	18.013	0.07
2	18	5	25.010	997.12	1834.50	9.151	9.1775	18.010	0.05
3	18	5	25.009	997.12	1806.05	9.006	9.0321	18.004	0.02
1	12	3.333	24.997	997.12	2708.95	9.014	9.0401	12.014	0.11
2	12	3.333	24.985	997.12	2723.95	9.054	9.0803	12.001	0.01
3	12	3.333	24.997	997.12	2868.50	9.540	9.5673	12.007	0.06
1	6	1.667	24.997	997.12	5419.46	9.010	9.0361	6.002	0.04
2	6	1.667	24.985	997.12	5404.60	8.981	9.0070	6.000	-0.01
3	6	1.667	25.009	997.12	5320.45	8.853	8.8785	6.008	0.13
1	1.2	0.333	24.994	997.12	9009.15	3.010	3.0184	1.206	0.51
2	1.2	0.333	25.045	997.11	9209.90	3.060	3.0686	1.199	-0.04
3	1.2	0.333	25.070	997.11	9095.85	3.010	3.0185	1.195	-0.45
1	0.6	0.167	25.033	997.11	12874.00	2.129	2.1348	0.597	-0.51
2	0.6	0.167	24.971	997.13	12700.89	2.117	2.1227	0.602	0.28
3	0.6	0.167	25.036	997.11	11905.68	1.974	1.9802	0.599	-0.21
1	0.3	0.083	24.997	997.12	16487.16	1.363	1.3666	0.298	-0.53
2	0.3	0.083	24.985	997.12	15840.48	1.308	1.3114	0.298	-0.66
3	0.3	0.083	25.082	997.10	15866.88	1.311	1.3144	0.298	-0.59
Overall AAPD									0.24

Table E2: Calibration of the Syringe Pump Using Syringe #616 (15.635 mmOD)

No of Run	f $ml \cdot h^{-1}$	$10^3 f$ $cm^3 \cdot s^{-1}$	t °C	ρ_{H2O} $kg \cdot m^{-3}$	Time sec	m_{H2O} g	V_{actual} ml	$f_{calibrated}$ $ml \cdot h^{-1}$	Error %
1	17.761	4.933	24.988	997.12	1794.28	8.844	8.8697	17.796	0.20
2	17.761	4.933	25.01	997.12	1780.79	8.788	8.8130	17.816	0.31
3	17.761	4.933	25.009	997.12	1776.42	8.753	8.7784	17.790	0.16
1	11.840	3.289	24.997	997.12	2694.83	8.849	8.8747	11.856	0.13
2	11.840	3.289	24.985	997.12	2837.07	9.309	9.3356	11.846	0.05
3	11.840	3.289	24.997	997.12	2838.96	9.327	9.3537	11.861	0.17
1	6	1.667	24.997	997.12	5367.38	8.894	8.9199	5.983	-0.29
2	6	1.667	24.997	997.12	5372.63	8.941	8.9671	6.009	0.14
3	6	1.667	24.985	997.12	5382.30	8.951	8.9771	6.004	0.07
1	1.2	0.333	24.994	997.12	9402.95	3.125	3.1336	1.200	-0.02
2	1.2	0.333	25.070	997.11	9245.14	3.070	3.0784	1.199	-0.11
3	1.2	0.333	24.985	997.12	9184.78	3.051	3.0593	1.199	-0.07
1	0.6	0.167	25.033	997.11	12942.29	2.139	2.1457	0.597	-0.53
2	0.6	0.167	24.971	997.13	12698.53	2.103	2.1095	0.598	-0.33
3	0.6	0.167	25.036	997.11	11919.97	1.981	1.9870	0.600	0.02
1	0.3	0.083	24.997	997.12	16453.28	1.357	1.3605	0.298	-0.78
2	0.3	0.083	24.985	997.12	15801.67	1.304	1.3073	0.298	-0.72
3	0.3	0.083	25.082	997.10	15837.56	1.306	1.3093	0.298	-0.80
Overall AAPD									0.27

To measure the excess molar enthalpies of ethanol(1)+*n*-hexane(2)+cyclohexane(3) mixture, it is necessary to obtain the calibration constants of the binary mixtures comprising of *n*-hexane (component 2) and cyclohexane (components 3) having fixed mole ratios in order to establish the relationship between the heat effect and the amplified thermoelectric output when there is no mixing of fluids. The experimental results of the calibration constants for three binary mixtures composed of *n*-hexane and cyclohexane at 25°C having *n*-hexane mole fraction of 0.25, 0.50, 0.75 are given in Figures E4 - E6, respectively.

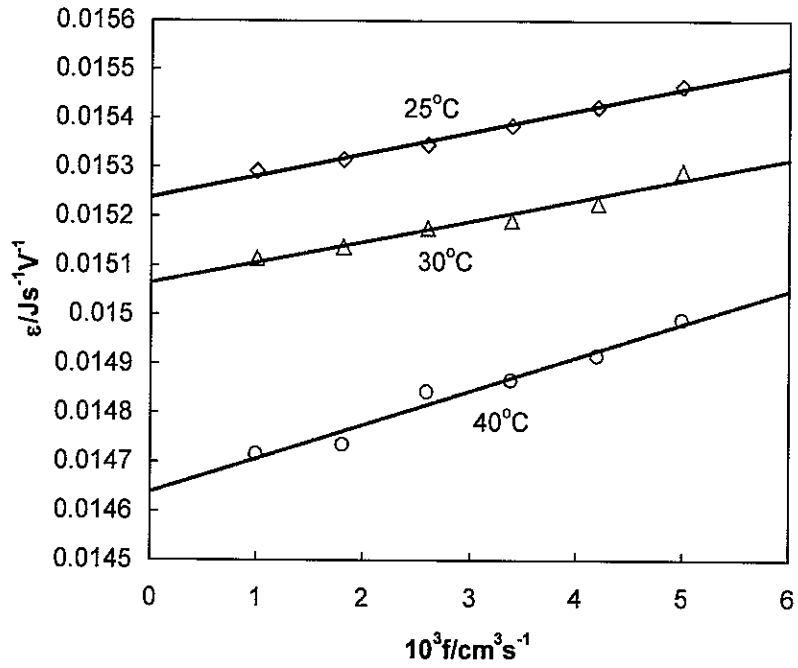

Figure E1: Variation of ε with f for Ethanol at 25, 30 and 40°C

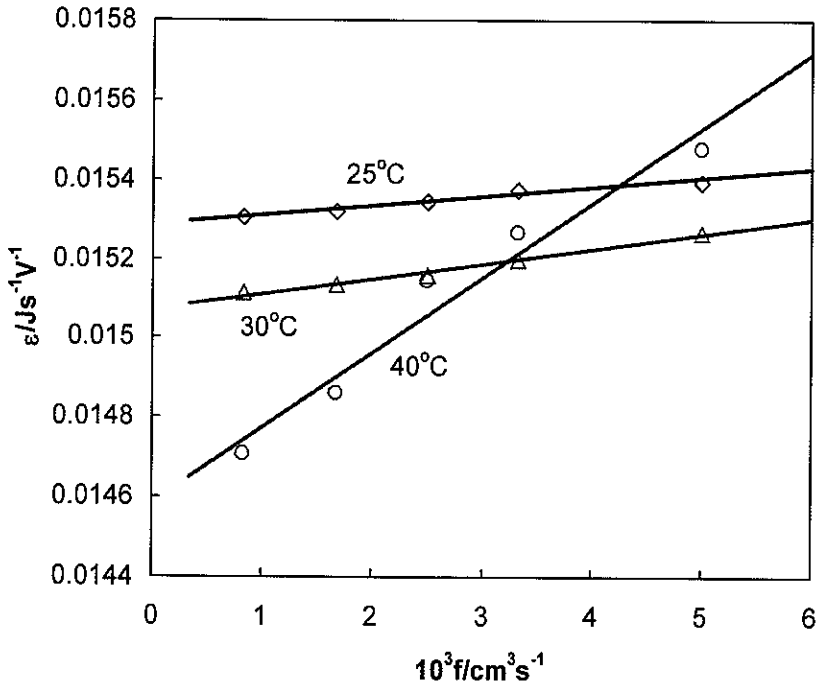

Figure E2: Variation of ε with f for *n*-Hexane at 25, 30 and 40°C

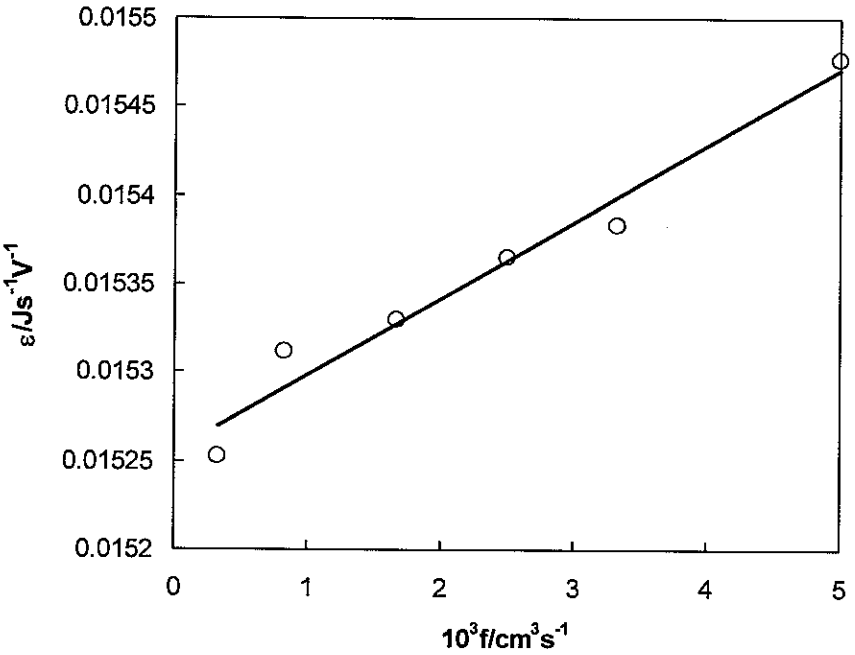

Figure E3: Variation of ε with f for Cyclohexane at 25°C

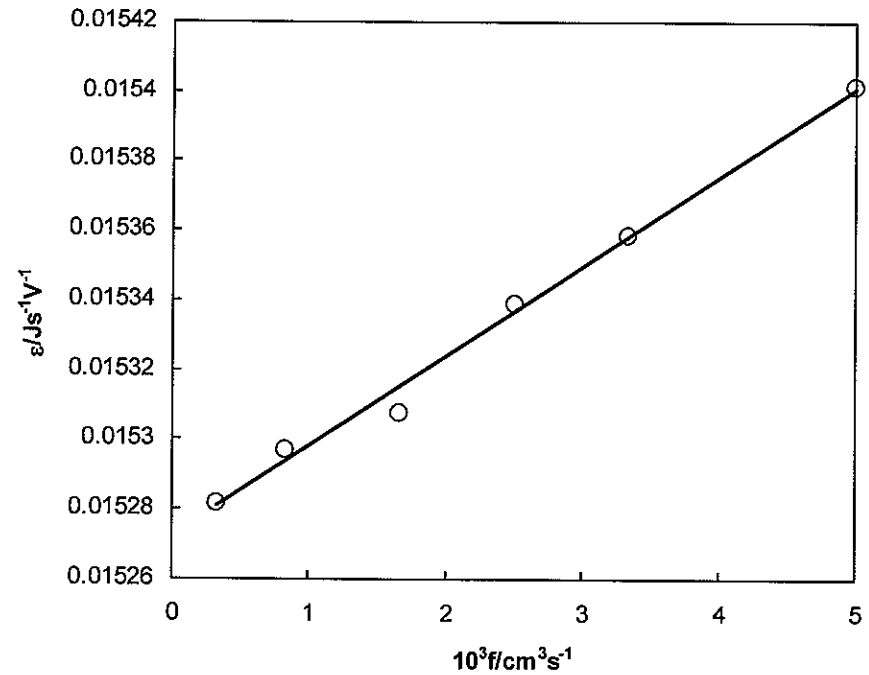

Figure E4: Variation of ε with f for *n*-Hexane(2)+Cyclohexane(3) System with x_2=0.25026 at 25°C

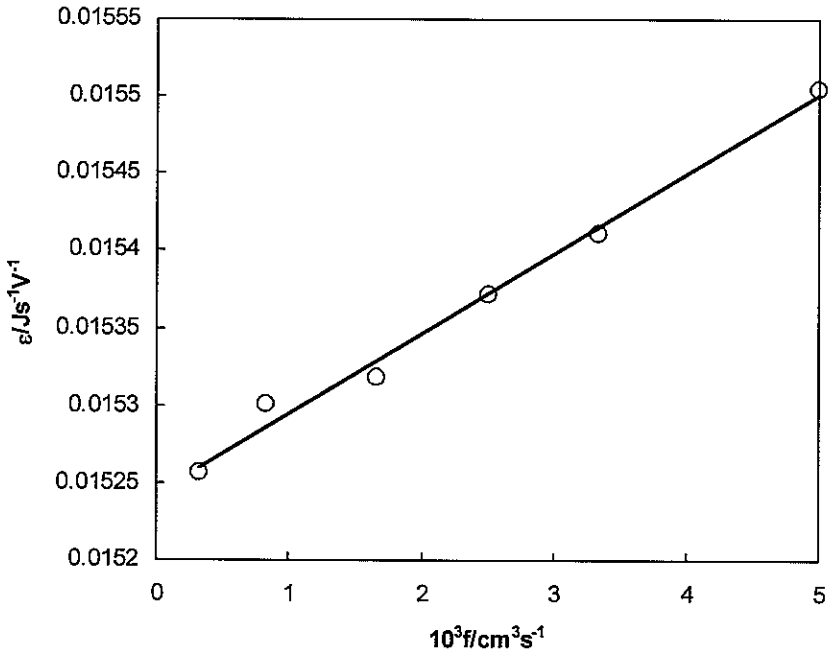

Figure E5: Variation of ε with f for *n*-Hexane(2)+Cyclohexane(3) System with x_2=0.49973 at 25°C

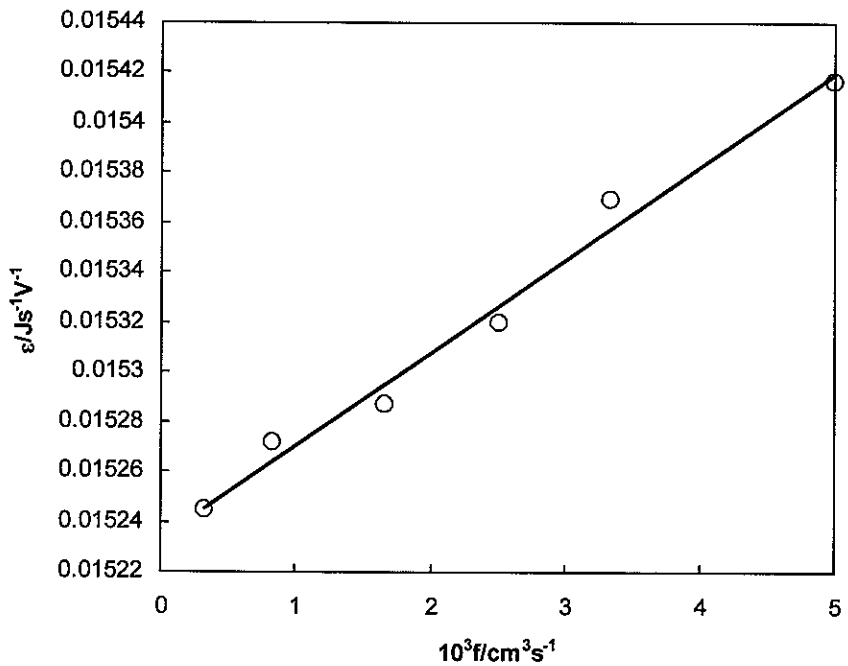

Figure E6: Variation of ε with f for *n*-Hexane(2)+Cyclohexane(3) System with x_2=0.74844 at 25°C

APPENDIX F
FIGURES OF SELECTED H^E CALCULATED RESULTS

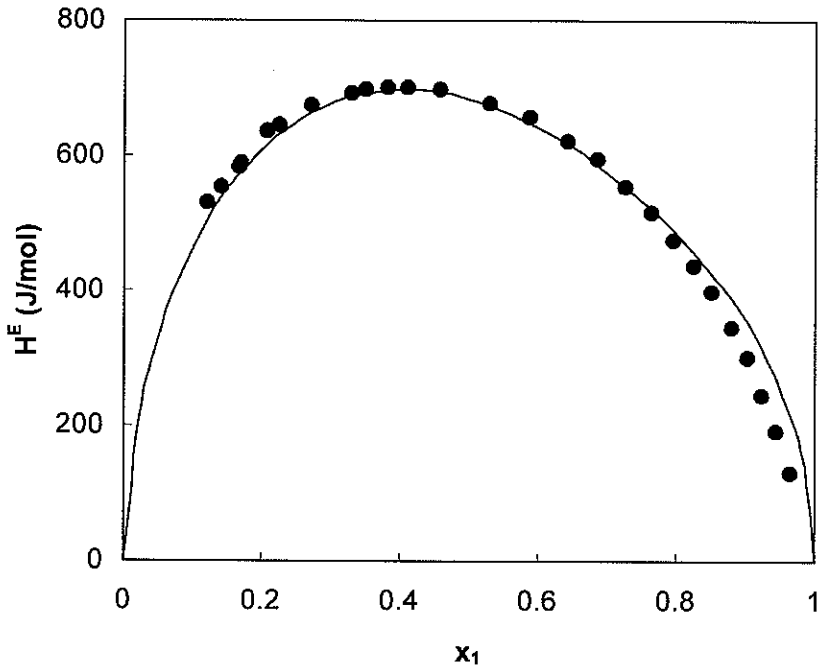

Figure F1: Excess Molar Enthalpies of Ethanol(1)+*n*-Nonane(2) System at 25°C and 170kPa. ●: Exp. (Christensen et al., 1979a); —: Cal.

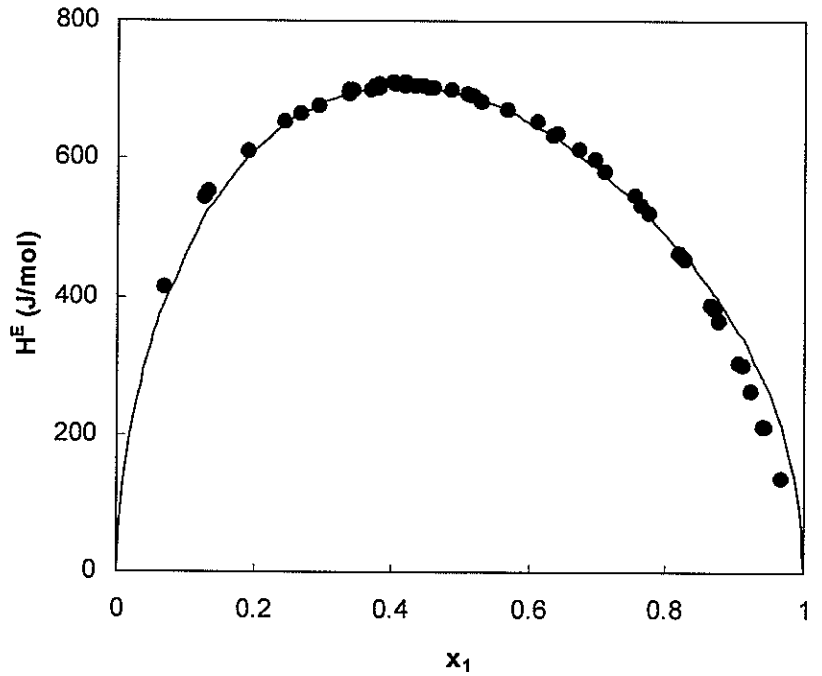

Figure F2: Excess Molar Enthalpies of Ethanol(1)+*n*-Decane(2) System at 25°C and 170kPa. ●: Exp. (Christensen et al., 1979b); —: Cal.

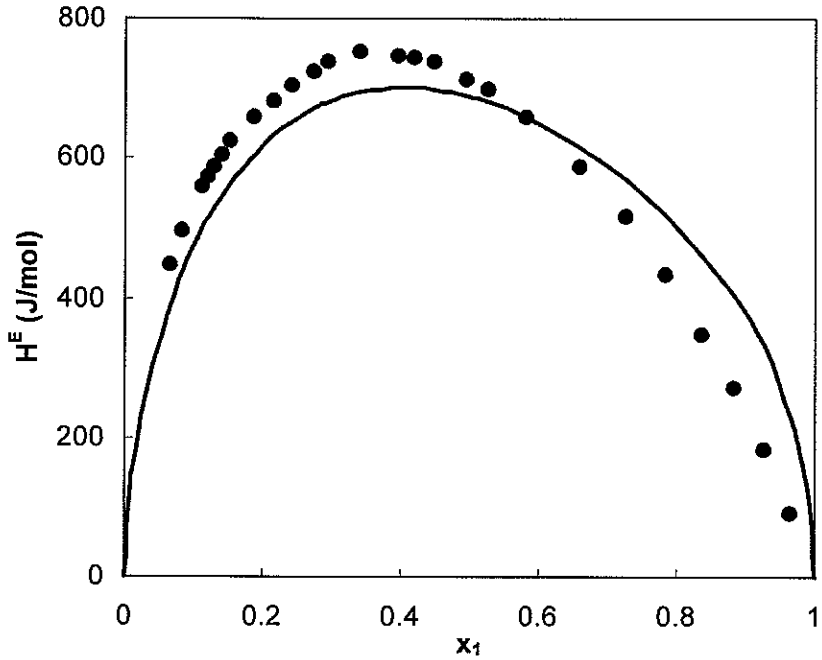

Figure F3: Excess Molar Enthalpies of 1-Propanol(1)+*n*-Nonane(2) System at 25°C and 170kPa. ●: Exp. (Christensen et al., 1979a); —: Cal.

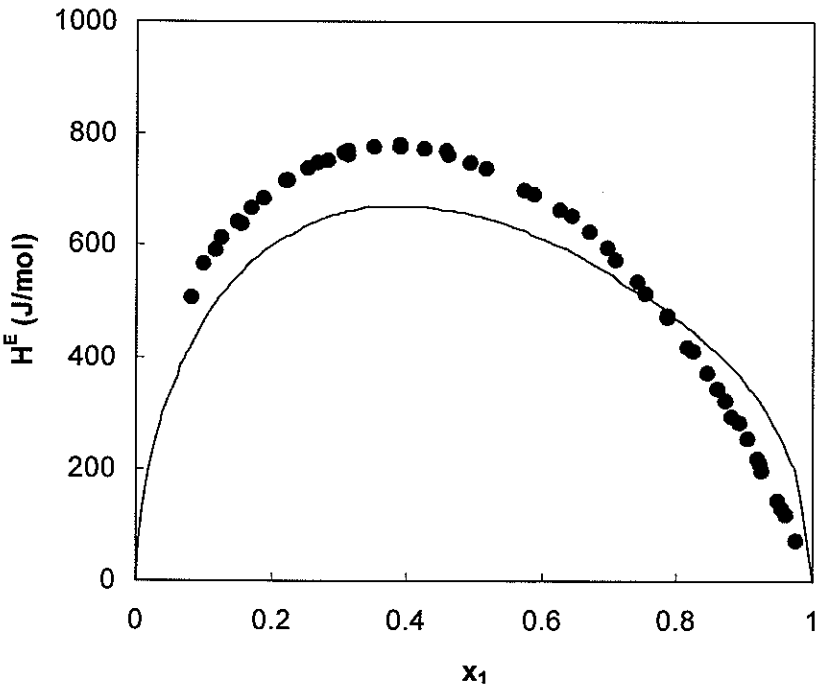

Figure F4: Excess Molar Enthalpies of 1-Propanol(1)+*n*-Decane(2) System at 25°C and 170kPa. ●: Exp. (Christensen et al., 1979b); —: Cal.

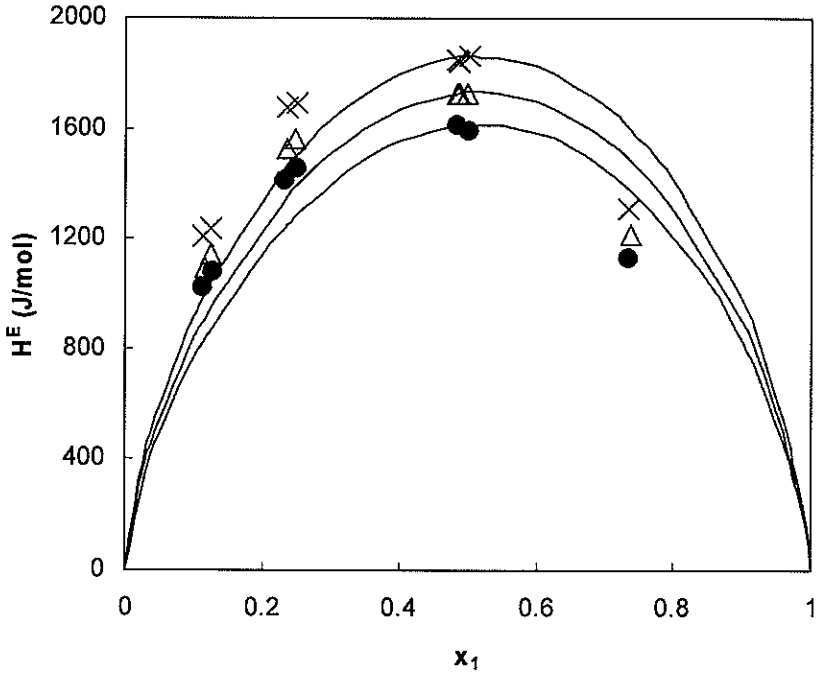

Figure F5: Excess Molar Enthalpies of 2-Butanol(1)+Benzene(2) System at 1atm. Exp. (Brown et al., 1969) ●: 25°C; Δ: 35°C; ×: 45°C; —: Cal.

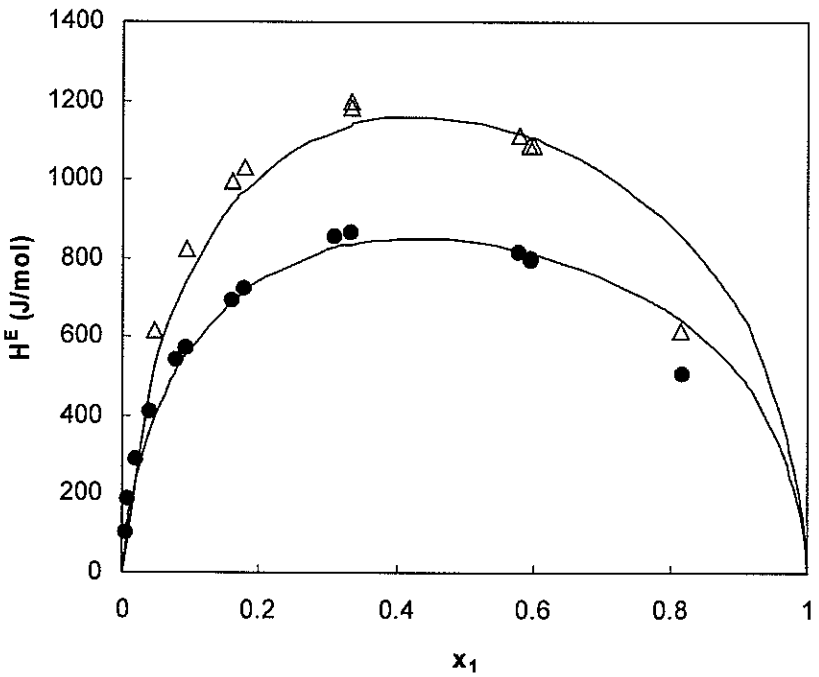

Figure F6: Excess Molar Enthalpies of 2-Butanol(1)+*n*-Hexane(2) System at 1atm. Exp. (Brown et al., 1969) ●: 25°C; Δ: 45°C; —: Cal.

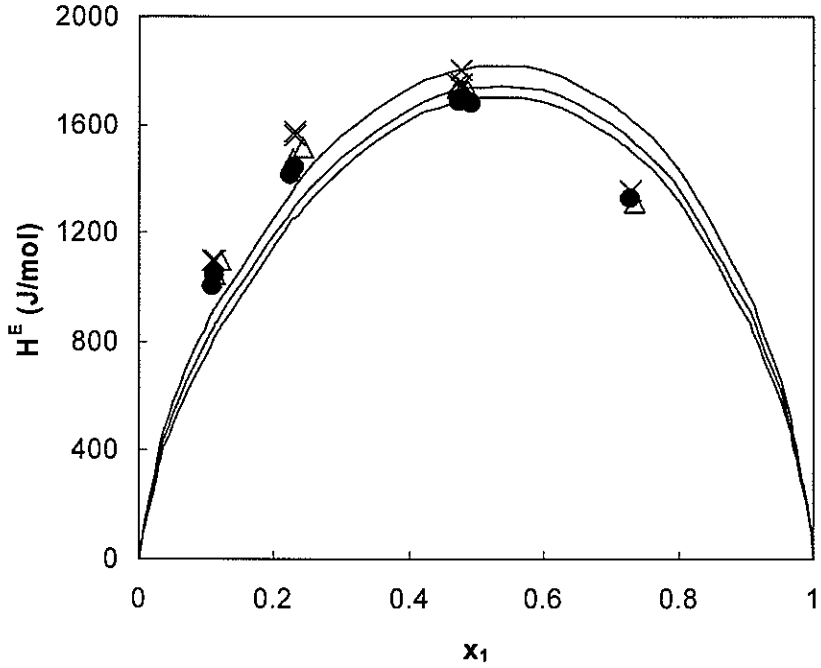

Figure F7: Excess Molar Enthalpies of Tert-butanol(1)+Benzene(2) System at 1atm. Exp. (Brown et al., 1969) ●: 27°C; Δ: 35°C; ×: 45°C; —: Cal.

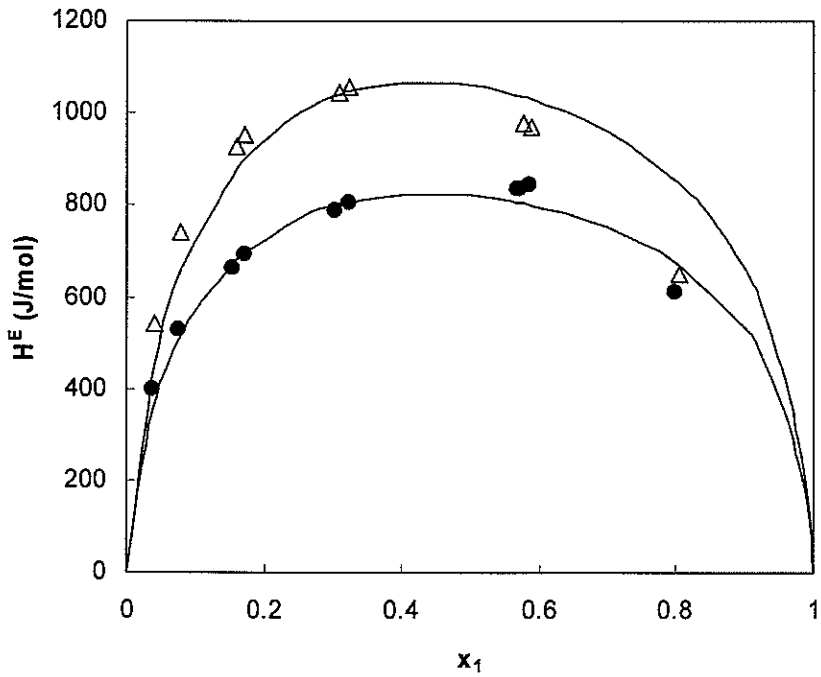

Figure F8: Excess Molar Enthalpies of Tert-butanol(1)+*n*-Hexane(2) System at 1atm. Exp. (Brown et al., 1969) ●: 27°C; Δ: 45°C; —: Cal.